THE USE OF TRIAZENES AS VINYL CATION PRECURSORS

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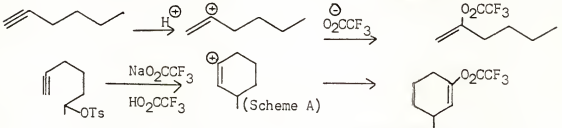
THE USE OF TRIAZENES AS VINYL CATION PRECURSORS

I. INTRODUCTION

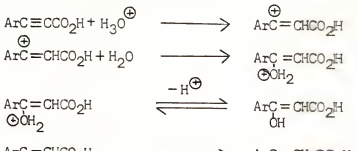
Within the past ten years several groups of investigators have studied reactions in which vinyl cations have been postulated as intermediates. The methods of access to vinyl cation intermediates can be conveniently divided into two general categories.

In the first method the vinyl cation is produced by the hydration of a triple bond. For example, Peterson (1) has postulated a vinyl cation in the reaction of 1-hexyne with trifluoroacetic acid, and in trifluoroacetolysis of 6-heptyn-2-yl p-toluenesulfonate (2) (Scheme A).



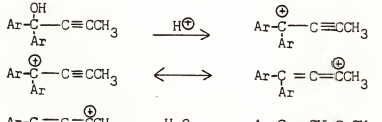
(Scheme A)

Noyce (3) has gathered product and kinetic evidence for the existence of a vinyl cation in the acid hydration of phenyl propiolic acids and phenyl acetylenes (Scheme B).



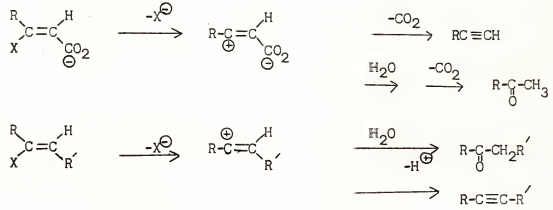
(Scheme B)

Richey (4) has presented spectral evidence for the existence of an unusual vinyl cation intermediate in a study of alkynyl cations (Scheme C).



(Scheme C)

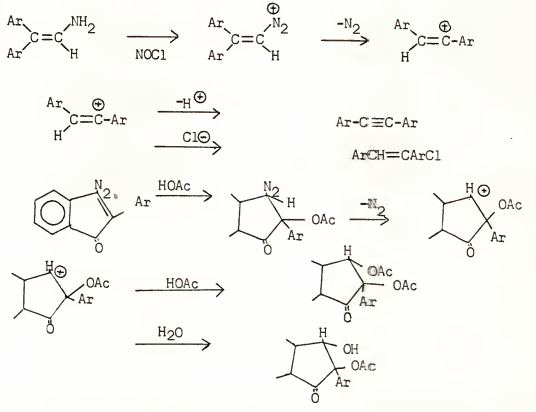
In the second general method the vinyl cation is produced by the loss of a vinylic halide ion or by the loss of elemental nitrogen from a vinyl diazonium ion. For example, Grob (5,6) has gathered evidence for the existence of a vinyl cation intermediate in the solvolytic decarboxylation of α,β-unsaturated β-halo acids and the solvolysis of bromo styrenes (Scheme D).



(Scheme D)

One of the better examples of this second route to the vinyl cation intermediate can be found in the recent work of Curtin (7) on the nitrosation of primary vinyl amines. Curtin postulated that the nitrosation produced a vinyl diazonium ion which decomposed to a

vinyl cation. The vinyl cation intermediate accounted for the products and yields under various reaction conditions. Curtin, however, found (8) that the products that were produced on nitrosation of 3-amino-2-phenylindenone were better explained by invoking an addition-elimination of acetic acid on the vinyl diazonium ion produced in the nitrosation (Scheme E).*



(Scheme E)

As a possible reason for the mechanistic change, Curtin suggested that the 1,2-diphenylvinyl cation could adopt a linear configuration but the analogous cation from the decomposition of the 3-diazonium-2-phenylindenone cation could not assume this linear configuration, and

* Product stereochemistry is not implied.

forced the decomposition to proceed through the observed addition-elimination mechanism. The concept that a linear vinyl cation is more stable than a non-linear vinyl cation because of charge delocalization is generally accepted (1-8 and references therein) and deserves little additional comment at this point.

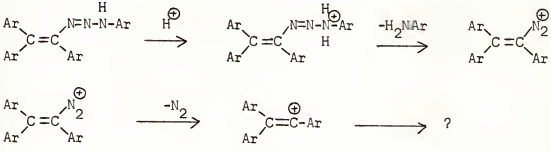
The change in mechanism which was inferred by Curtin (8) has serious implications. A study of any system in which a vinyl cation is postulated as a possible intermediate must also include evidence designed specifically to rule out a possible addition-elimination route to products.

In light of the recent success of Curtin, it was decided that a study of vinyl cations using vinyl diazonium ion precursors might prove even more fruitful if a wider variety of vinyl diazonium ions were available and if the scope of the mechanistic study could be broadened by making solvent changes. Several problems became evident. First, aryl vinyl amines are not a well known class of compounds and aliphatic vinyl amines are not synthetically accessible. Second, the fact that the diazonium ion is generated and destroyed in situ automatically limits the choice of solvents and conditions under which the vinyl cation can be studied.

There is some evidence that the decomposition of phenyl diazonium ions in polar media can lead to the formation of phenyl cations (9,10), which are formally analogous to vinyl cations. Furthermore, aryl triazenes have long been known to undergo rearrangements and decomposition reactions that are explained on the basis of diazonium intermediates (11). The synthesis of a series of vinyl triazenes was therefore under-

taken for use as possible precursors of vinyl diazonium ions. The method chosen for the synthesis was a standard triazene preparation method consisting of the treatment of a Grignard reagent with phenyl azide, followed by hydrolysis using ammonium chloride-ammonia (12).

It was hoped that the acid-induced triazene decomposition would lead to vinyl cations as shown below. (Scheme F).* In addition to gathering evidence for the existence of a vinyl cation intermediate through



(Scheme F)

a systematic study of various substituted triazenes, experiments were designed to eliminate the possibility of an addition-elimination mechanism that could explain the products. Finally, the study was designed to explore the chemistry of vinyl cation intermediates and their potential synthetic utility.

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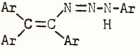
* Although tautomerism prevents the fixing of the nitrogen double bond chemically (11), only one of the two possible isomeric structures will be used throughout this study to represent the pair of tautomeric triazenes.

II. THE SYNTHESIS AND DECOMPOSITION OF 1-(TRIPHENYLETHENYL)-3-PHENYL-1-TRIAZENE

The synthesis of 1-(triphenylethenyl)-3-phenyl-1-triazene (I) was accomplished by treating an ethereal solution of triphenylvinyl magnesium bromide with phenyl azide. The Grignard intermediate was hydrolyzed by the addition of ammonium chloride-ammonia solution to the reaction. After separation and drying of the organic layer and removal of the ether with a stream of nitrogen, an oil remained which was dissolved in pentane. Refrigeration of the pentane solution gave yellow crystals of 1-(triphenylethenyl)-3-phenyl-1-triazene in good yield.



(I)

The elemental analysis of the triazene agreed with the required empirical formula. The infrared (IR) spectrum exhibited peaks at 3.0, 3.3 and 6.3 μ., compatible with the proposed structure. Ozonolysis of the triazene produced benzophenone, which shows that the compound has the indicated carbon double bond and eliminates the possibility that the material has a cyclic 4,5-dihydro-1,2,3-triazoline structure.

The results of the triazene decomposition with a variety of acids and acid-salt buffers are summarized in Table I.*

* Although no rigorous kinetic work was done, a plot of reaction time vs. ml. of nitrogen evolved was made for the decomposition of all of the triazenes used in this study in various media. The points invariably fit

Treatment of 1-(triphenylethenyl)-3-phenyl-1-triazene with dry acetic acid at room temperature led to the smooth evolution of the theoretical amount of nitrogen within one minute. No induction period was observed. The solvent was removed leaving two solids which were separated by fractional crystallization from petroleum ether. The first had an IR spectrum that was superimposible on a spectrum of authentic triphenylvinyl acetate (II), and accounted quantitatively for the triphenylvinyl entity. The second compound quantitatively accounted for the aniline entity and was compared to authentic acetanilide using IR and found to be identical.

(II)

A sample of aniline gave acetanilide quantitatively when treated with the reaction solvent at room temperature. Trace amounts of acetic anhydride in the dry acetic acid reaction medium, resulting from the distillation of acetic acid from acetic anhydride, accounted for the formation of acetanilide under reaction conditions.

A sample of the triazene was added to cold 98 percent sulfuric acid. After gas evolution had ceased, the mixture was poured over ice and extracted well with ether. The ether layer was washed with water and dried. After removal of the ether, a solid was obtained that had

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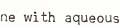
a smooth curve to better than 80 percent reaction. The line had its origin at zero time, in the presence or absence of oxygen, which argues against a radical decomposition mechanism.

an IR spectrum that exhibited all of the peaks present in a spectrum of phenyl benzhydryl ketone. In addition, thin layer chromatography (TLC) showed the presence of a material with an R_F value identical to that of authentic phenyl benzhydryl ketone.

When a sample of the triazene was treated with cold sulfuric acid and the mixture was poured into a cold slush of glacial acetic acid and again extracted into ether, an IR spectrum of the mixture after removal of the ether exhibited all of the peaks present in a phenyl benzhydryl ketone spectrum and also all of the peaks present in an IR spectrum of triphenylvinyl acetate. Finally, TLC showed the presence of materials with R_F values of both of these compounds.

Decomposition of the triazene with aqueous fluoboric acid at room temperature afforded excellent yields of phenyl benzhydryl ketone (III). The IR spectra of the triazene decomposition ketone and an authentic sample were identical.



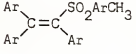
(III)

Decomposition of the triazene with p-toluenesulfonic acid-sodium p-toluenesulfonate and dimethyl sulfoxide as the reaction medium led to the production of triphenylvinyl p-toluenesulfonate (IV). The elemental analysis agreed with the required empirical formula, the IR spectrum was compatible with the proposed structure and the material hydrolyzed quantitatively to phenyl benzhydryl ketone and p-toluenesulfonic acid when treated with aqueous alcoholic hydrochloric acid.

(IV)

In addition to the triphenyl vinyl p-toluenesulfonate found in this reaction, a moderate percentage of phenyl benzhydryl ketone was found. The identity of the latter was proved by IR comparison to an authentic sample.

The decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene with p-toluenesulfinic acid-sodium p-toluenesulfinate in dimethylformamide at room temperature gave an oil that is probably triphenylvinyl p-tolyl-sulfone (V). The oil exhibited IR peaks at 6.3, 7.5, 8.8 and 9.0 μ., which are characteristic of a vinyl sulfone.



(V)

Moderate amounts of phenyl benzhydryl ketone were found in this triazene decomposition in addition to the presumed triphenylvinyl p-tolyl-sulfone. An IR spectrum of the phenyl benzhydryl ketone was superimposible on a spectrum of authentic sample.

A sample of triazene was cooled to dry ice temperatures and treated with an ethereal solution of phenol in an attempt to trap the triphenyl diazonium ion, a postulated decomposition intermediate. The reaction mixture was warmed to 0° and, after the reaction was complete, it was analysed for products. Good yields of triphenylvinyl phenolate (VI) were found.

(VI)

The material had an elemental analysis that agreed with the required empirical formula and an IR spectrum of the compound was compatible with the proposed structure.

TLC showed very small amounts of two additional compounds to be present. A separate experiment, run with the same reagents at room temperature, gave quantitative nitrogen evolution, good yields of triphenylvinyl phenolate and very small amounts of the same two additional compounds. Neither of the two compounds could have contained a diazonium linkage since nitrogen evolution had been complete. In addition, the decomposition which was run at low temperature, where diazonium ion capture could have been more probable, gave the same two additional products as the reaction which was run at room temperature. Therefore, it is unlikely that either of the two minor compounds would give information about the diazonium ion intermediate.

The triphenylvinyl diazonium ion intermediate was not intercepted under the experimental conditions used here. A possible mechanistic implication of this experimental finding is that the triphenylvinyl diazonium ion that is produced in the decomposition is short-lived and the triphenylvinyl system does not provide the combined stabilization of the diazonium ion and the destabilization of the cation resulting from the loss of nitrogen which are required for the isolation of a stable diazonium ion, under the experimental conditions employed in this reaction.*

* Similar results were obtained for the diphenyl diazonium ion in this study and by Curtin (7).

The potential synthetic utility of the triphenyl triazene is evident. A wide variety of tetra-substituted vinyl compounds are available from this single triazene by merely changing the decomposition medium. The excellent yields of phenyl benzhydryl ketone produced in the aqueous acid decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene make the triazene method a good method for synthesizing this compound also.

Since the only difficulty in the triazene method of synthesizing vinyl compounds lies in the isolation and purification of the triazene, an ethereal solution of the crude triazene was treated with dry acetic acid directly. The isolable yield of triphenylvinyl acetate was 85 percent based on the starting triphenylvinyl bromide.*

Although it is tempting at the outset to postulate that the acid decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene proceeded through a triphenylvinyl cation intermediate on the basis of the sulfuric acid decompositions alone (4),+ the vinyl cation mechanism is not required for the formation of the products found in the other decompostion media. The addition-elimination mechanism shown below could be

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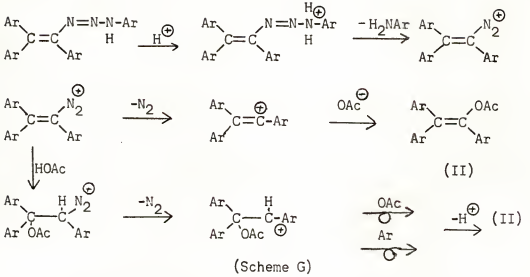
* Anhydrous conditions are important since phenyl benzhydryl ketone is formed preferentially if water is present. Phenyl benzhydryl ketone can be recovered quantitatively from the acetic acid reaction medium and does not yield triphenylvinyl acetate under reaction conditions. Triphenylvinyl acetate also can be recovered quantitatively from the acetic acid reaction medium and does not yield phenyl benzhydryl ketone under reaction conditions.

+ For lead references on the interpretation of similar data see the recent work of Olah (13).

used to rationalize the other products (Scheme G).



(Scheme G)

This mechanism was postulated by Curtin (8) to explain the exclusive production of 1,2-diacetates and 1,2-hydroxy-acetates in the nitrosation of 3-amino-2-phenylindenone (Scheme E). Only one piece of evidence argues against this mechanism in the acid triazene decomposition. No diacetates or hydroxy-acetates were found in the acetic acid decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene.*

To make an unequivocal choice between the two possible pathways, some type of label must be incorporated to distinguish between the two vinyl carbon atoms, and the decomposition must be run in the presence of a nucleophile that cannot rearrange through an "onium ion" (VII) intermediate.

* A sample of triphenylethyleneglycol diacetate was found to be stable to reactions conditions.

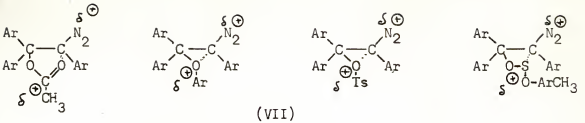
TABLE 1

DECOMPOSITION OF 1-(TRIPHENYLETHENYL)-3-PHENYL-1-TRIAZENE

Decomposition medium (a)	Time for total gas evolution	Products and percent yields
7 ml. glacial acetic acid	seconds	triphenylvinyl acetate (II), 100 (b)
7 ml. of 10 percent aq. fluoboric acid	seconds	phenyl benzhydryl ketone (III), 100
5 mol. eq. p-toluene sulfonic acid hydrate, 5 mol. eq. sodium p-toluene sulfonate hydrate, 7 ml. dimethyl sulfoxide	three hours	triphenylvinyl p-toluene sulfonate (IV), 20; phenyl benzhydryl ketone (III), 80
5 mol. eq. p-toluene sulfinic acid hydrate, 5 mol. eq. sodium p-toluene sulfinate hydrate, 7 ml. dimethylformamide	ten hours	triphenylvinyl p-tolyl-sulfone (V), 45; phenyl benzhydryl ketone (III), 55
10 mol. eq. phenol 7 ml. ether	ten minutes	triphenylvinyl phenolate (VI), 65; phenyl benzhydryl ketone (III), 35

a. All reactions were run at room temperature using 0.5000 g. of triazene.

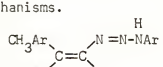
b. Acetanilide was also isolated.



(VII)

Although labeling of the vinyl carbon atoms is feasible, either by appropriate substitution of the aryl groups on the vinyl carbon atoms or by the use of isotopes, a diligent search for a nucleophile that cannot rearrange through an "onium ion" proved fruitless. All of the nucleophiles that were used for the acid decompositions of 1-(triphenylethenyl)-3-phenyl-1-triazene can rearrange through an "onium ion" except the sulfinate ion. Sulfinate ions are ambivalent (14,15,16) and the mechanistic exclusion of the sulfinate-sulfone rearrangement could be difficult.

As a possible method to further clarify the mechanism of the acid decomposition of the vinyl triazenes as well as to explore the scope of the reaction, 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene (VIII), 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene (IX) and 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene (X) were synthesized. Hopefully, a consideration of the rearranged and non-rearranged products of the acetic acid decompositions would provide a further distinction between the two mechanisms.



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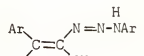

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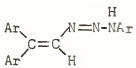
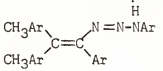


(X)

III. THE SYNTHESIS AND DECOMPOSITION OF 1-(2,2-DI-P-TOLYL-PHENYLETHENYL)-3-PHENYL-1-TRIAZENE

The synthesis of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene (VIII) was accomplished by treating an ethereal solution of 2,2-di-p-tolylphenylvinyl magnesium bromide with phenyl azide.

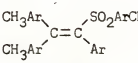


(VIII)

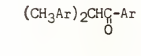
Its structure was confirmed by elemental analysis and by its IR spectrum, which was compatible with the proposed structure. Ozonolysis of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene produced a compound that had an IR spectrum that was superimposible on an IR spectrum of authentic di-p-tolyl ketone.* Gas chromatography (GLC) of the ozonolysis product showed the presence of a compound that had a retention time identical to that of authentic di-p-tolyl ketone, but no peak was present that had a retention time identical to that of p-methylbenzophenone. The results of the ozonolysis indicate that the triazene has both p-tolyl groups attached to the terminal vinyl carbon atom and also rule out the possibility that the new material has a cyclic triazoline structure.

* Random analytical checking showed that the ozonolysis of the vinyl compounds in the study gave greater than 90 percent of the predicted ketones regularly.

The decomposition of the triazene with p-toluenesulfinic acid hydrate-sodium p-toluenesulfinate hydrate buffer in dimethylformamide at room temperature gave an oil that is probably 2,2-di-p-tolylphenylvinyl p-tolyl-sulfone (XI) in 20 percent yield, and phenyl di-p-tolyl ketone (XII) in 80 percent yield.



(XI)

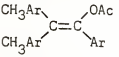


(XII)

The IR spectrum of the sulfone (XI) exhibited peaks at 6.3, 7.5 and 8.7 μ., which is compatible with the proposed structure. The sulfinate decomposition reaction mixture was poured into water and the organic material was thoroughly extracted with ether. Ozonolysis of the organic material gave di-p-tolyl ketone, identified by IR comparison to an authentic sample. GLC showed the presence of a material that had a retention time identical to that of authentic di-p-tolyl ketone but no material was present that had a retention time identical to that of authentic p-methylbenzophenone. An amount of p-methylbenzophenone corresponding to 1 percent of the di-p-tolyl ketone present was easily identified by GLC. A sample of phenyl di-p-tolyl ketone was submitted to ozonolysis conditions and found to be stable. GLC of the phenyl di-p-tolyl ketone ozonolysis stability test showed no peak present that had a retention time identical to that of authentic di-p-tolyl ketone. The results of the ozonolysis of the sulfinate decomposition reaction exclude the possible formation of the isomeric 1,2-di-p-tolylphenylvinyl p-tolyl-sulfone in this decomposition.

The phenyl di-p-tolyl ketone (XII) produced in the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with sulfinic acid-sulfinate hydrate buffer had an IR spectrum that was nearly superimposible on an IR spectrum of phenyl benzhydryl ketone.

The decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with acetic acid-potassium acetate buffer at room temperature gave quantitative 1,1-di-p-tolylphenylvinyl acetate (XIIIa) and acetanilide.



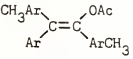
(XIIIa)

The identity of the latter was established by IR comparison to an authentic sample of acetanilide. The elemental analysis of 2,2-di-p-tolylphenylvinyl acetate agreed with the required empirical formula. An IR spectrum of the vinyl acetate exhibited peaks at 3.3, 5.7 and 8.3 μ., which is compatible with the proposed structure.

The acetate decomposition reaction was poured into water and thoroughly extracted with ether. Ozonolysis of the organic material gave di-p-tolyl ketone, identified by IR comparison to an authentic sample. GLC showed the presence of no material that had a retention time identical to that of authentic p-methylbenzophenone. A sample of authentic acetanilide was submitted to ozonolysis conditions and found to be stable. The possible presence of 1,2-di-p-tolylphenylvinyl acetate in the acetic acid-potassium acetate buffer is excluded by the results of the ozonolysis.

The decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with pure acetic acid at room temperature led to quantitative production of two isomeric di-p-tolylvinyl acetates and a material that

had an IR spectrum that was superimposible on a spectrum of authentic acetanilide.



(XIIIb)

The isomeric acetate mixture (XIIIa,XIIIb)* exhibited IR peaks at 3.3, 5.7 and 8.3 μ., which is compatible with the proposed structures. The elemental analysis of the isomeric mixture agreed with the required empirical formula. The reaction mixture was concentrated at room temperature under vacuum, was dissolved in ethyl acetate, ozonized and analysed by GLC.+ Two components were present in the ratio of 4:1. The major component had a retention time identical to that of authentic di-p-tolyl ketone. The minor component had a retention time identical to that of authentic p-methylbenzophenone. An IR spectrum of the ozonolysis mixture was compatible with a spectrum of a mixture of authentic samples. The results of the ozonolysis indicate that the major acetate produced by the acetic acid decomposition of 1-(di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene was 2,2-di-p-tolylphenylvinyl acetate (XIIIa), and the minor acetate produced by the acid decomposition was 1,2-di-p-tolyl-phenylvinyl acetate (XIIIb).

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* The cis-trans stereochemistry of this compound was not determined.
+ Within five minutes, the color of the reaction mixture indicated that ozonolysis was complete. Ozone was passed through the solution for an additional ten minutes.

The decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with an ethereal solution of acetic acid at room temperature led to the quantitative production of 2,2-di-p-tolylphenylvinyl acetate (XIIIa), and 1,2-di-p-tolylphenylvinyl acetate (XIIIb). The decomposition also afforded a material that had an IR spectrum that was superimposible on a spectrum of authentic acetanilide.

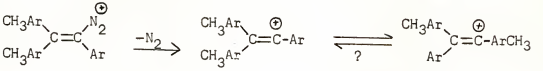
The isomeric acetate mixture exhibited IR peaks at 3.3, 5.7 and 8.3 μ., which is compatible with the proposed structures. The decomposition reaction was concentrated under vacuum, ozonized and analysed by GLC. Two components were present in the ratio of 3:8:1. The major component had a retention time that was identical to that of authentic di-p-tolyl ketone. The minor component had a retention time that was identical to that of authentic p-methylbenzophenone. An IR spectrum of the mixture was compatible with the spectrum of a mixture of authentic samples. The results of the ozonolysis indicate that the major acetate produced by the ethereal acetic acid decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene was 2,2-di-p-tolyl-phenylvinyl acetate (XIIIa), and the minor acetate produced by the acid decomposition was 1,2-di-p-tolylphenylvinyl acetate (XIIIb).

Although the experimental evidence in the acid decompositions of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene does not allow a distinction between the vinyl cation mechanism and addition-elimination (Scheme G), the results are remarkably consistent with a vinyl cation intermediate.* Furthermore, the results of the sulfuric acid decompositions

* Direct nucleophilic displacement of nitrogen by acetate cannot be the exclusive pathway to products since it cannot explain the rearranged products found throughout this study.

of the triphenyl triazene present rather compelling evidence for the existence of this analogous vinyl cation.

Consider the decomposition in the presence of sulfinate ion, where no rearranged product is found and the glacial acetic acid decomposition, where 20 percent rearranged product is found. Since the sulfinate ion is a much better nucleophile that acetic acid (17), the experimental results are in accord with an attack by sulfinate on the vinyl cation before it can rearrange while acetic acid, the poorer nucleophile, gives products from a partially rearranged pair of cations (Scheme H).



nucleophile

non-rearranged product

rearranged product

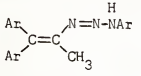
(Scheme H)

Consider the decomposition in the presence of acetic acid-potassium acetate buffer and the decomposition in pure acetic acid. Since the acetate ion is a better nucleophile than acetic acid, and the concentration of acetic acid is less in ethereal acetic acid than in pure acetic acid, the vinyl cation mechanism requires less rearrangement in the former and more in the latter (Scheme H).

The experimental findings fulfill this mechanistic requirement. The decomposition in the presence of acetate buffer yielded no rearranged product. It is interesting that the decomposition in the presence of pure acetic acid led to only slightly less rearranged product than the decomposition in ethereal acetic acid.

IV. THE SYNTHESIS AND DECOMPOSITION OF 1-(2,2-DIPHENYL-METHYLETHENYL)-3-PHENYL-1-TRIAZENE

The synthesis of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene was accomplished by treating an ethereal solution of 2,2-diphenylmethyl-vinyl magnesium bromide with phenyl azide.



(IX)

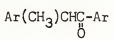
The low stability of the triazene prevented an elemental analysis, but the IR spectrum of the material exhibited peaks at 3.0, 3.3 and 6.25 μ., although the heat generated by the IR source had a tendency to decompose the material. Ozonolysis of the compound gave benzophenone, which was identified by comparison of the IR spectrum of the ozonolysis product and benzophenone. GLC showed the presence of a compound that had a retention time identical to that of authentic benzophenone, but no material was present in the ozonolysis product that had a retention time identical to that of acetophenone, which shows that the triazene has both aryl groups attached to the terminal vinyl carbon atom and also rules out the possibility that the new compound has a cyclic triazoline structure.

The decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene with acetic acid at room temperature led to the production of 1,2-diphenylmethylvinyl acetate (XIVa) (87%), 2,2-diphenylmethylvinyl

acetate (XIVb) (5.8%), α-phenylpropiophenone (XV) (8.7%) and a compound that had an IR spectrum that was superimposible on a spectrum that was superimposible on a spectrum of authentic acetanilide. GLC check on the material balance showed that less than 1 percent of 1,1-diphenylacetone could have been formed in the decomposition.

(XIVa)*

(XIVb)



(XV)

GLC showed that the three new components were present in a ratio of 25:2:3 respectively. An IR spectrum of the crude decomposition products after the removal of the acetic acid under vacuum, exhibited peaks at 3.3, 3.5, 5.7, 6.25 and 8.3 μ., which is compatible with a vinyl acetate compound. Ozonolysis of the crude acetic acid decomposition reaction gave a four component mixture. GLC showed that one of the components had a retention time identical to that of authentic acetanilide. Acetanilide was subsequently shown to be stable to ozonolysis conditions, and the conditions under which the ozonide was decomposed. A second component formed in the ozonalysis had a retention time identical to that of one of the minor components in the original acetic acid decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene and was later shown to be α-phenylpropiophenone.

The final two components of the ozonolysis were present in a ratio of 10:1 and had retention times that were identical to those of authentic samples of acetophenone and benzophenone respectively. An IR spectrum of the crude ozonolysis product was compatible with a

* The cis-trans stereochemistry of this compound was not determined.

spectrum of acetophenone.

The results of the ozonolysis indicate that the major acetate produced in the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene with acetic acid was 1,2-diphenylmethylvinyl acetate (XIVa). The minor acetate produced in the decomposition was 2,2-diphenylmethylvinyl acetate (XIVb).

A sample of the crude mixture from the decomposition of the triazene was treated with hot ethanolic aqueous hydrochloric acid for three hours. The reaction mixture was poured into water and extracted thoroughly with ether. The ether layer was washed with dilute acid and base and dried. The ethereal solution was concentrated to an oil, whose weight represented an 89 percent recovery of the diphenylmethylvinyl entity.

The product of the reaction that was insoluble in dilute acid and dilute base had an IR spectrum that exhibited a peak at 5.95 μ., which is compatible with a phenyl ketone and a minor carbonyl peak at 5.8 μ. which may indicate trace contamination by 1,1-diphenylacetone. The proton magnetic resonance spectrum (NMR) of the phenyl ketone exhibited a multiplet at 2.75τ, a quartet at 5.32τ and a doublet at 8.47τ, which is compatible with α-phenylpropiophenone (XV). In addition, the hydrolysis ketone gave a peak of identical retention time to that of one of the minor components of the decomposition of the triazene with acetic acid, when subjected to GLC. A sample of α-phenylpropiophenone produced in the hydrolysis of the decomposition mixture of the triazene was submitted to ozonolysis conditions, and quantitatively recovered. GLC of the ozonolysis product showed the presence of a peak with retention time identical to that of the hydrolysis ketone, but no peaks

were present that had retention times identical to those of authentic benzophenone and acetophenone. The IR spectrum of the α-phenylpropiophenone that was recovered from the ozonolysis conditions and a spectrum of the original α-phenylpropiophenone from the acetate hydrolysis were superimposible.

The results of the ozonolysis of the products of the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene with acetic acid and the results of the hydrolysis of the acetic acid decomposition products present strong evidence for the structures (XIVa,b,XV) of the acetic acid decomposition products of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene.

Thus, the acetic acid decomposition of this triazene led to the production of 1,2-diphenylmethylvinyl acetate, 2,2-diphenylmethylvinyl acetate and α-phenylpropiophenone.

Although the experimental data gathered in the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene with acetic acid do not allow a distinction between the vinyl cation mechanism and the addition-elimination mechanism (Scheme G), the results at this point in the study support a vinyl cation intermediate.

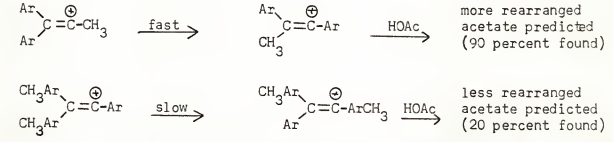
Consider the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene in acetic acid, which led to products that were greater than 90 percent rearranged, and the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene in acetic acid, which led to products that were only 20 percent rearranged.

Since a methyl group is less effective than a phenyl in stabilizing

a positive charge on an adjacent carbon atom (18), the vinyl cation resulting from the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene could be less stable than the vinyl cation from the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene.

A competition between acetate attack before rearrangement and cation rearrangement exists and the methyl cation could be expected to have more tendency to rearrange than the di-tolyl cation. Thus, the di-tolyl cation rearrangement may be less profitable energetically than the rearrangement of the di-phenyl methyl cation would give more rearranged acetate and the di-tolyl cation should give less rearranged acetate. The experimental results support this prediction (SchemeI).*

Furthermore, the compelling evidence gathered in the sulfuric acid decomposition of the triphenyl triazene again reinforce the vinyl cation possibility.

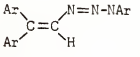


(Scheme I)

* The percentages of rearranged and non-rearranged acetates found in the decomposition of these triazenes are further discussed in VI and found to be inconsistant with an addition-elimination mechanism (Scheme G).

V. THE SYNTHESIS AND DECOMPOSITION OF 1-(2,2-DIPHENYLETHENYL)-3-PHENYL-1-TRIAZENE

The synthesis of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene (X) was accomplished by treating an ethereal solution of 2,2-diphenylvinyl magnesium bromide with phenyl azide. Its structure was confirmed by analysis, by its IR spectrum, which was compatible with the proposed structure and by ozonolysis to benzophenone, which eliminated the possible triazoline structure.



(X)

The products of the decomposition of this triazene using a variety of acetate ion concentrations are summarized in Table II. Under all of the experimental conditions listed, the decomposition gave high yields of diphenylacetylene (XVI) and moderate yields of desoxybenzoin (XVII).

(XVI)

(XVII)

The identity of the reaction products was established by IR comparison to authentic samples. In the presence of added potassium acetate or high concentrations of acetic acid, two additional products were found. The first is believed to be cis-1,2-diphenylvinyl acetate (XVIII). The second, present in very small amounts is believed to be

trans-1,2-diphenylvinyl acetate (XIX).*

(XVIII)

(XIX)

No diphenylacetaldehyde, 2,2-diphenylvinyl acetate or hydrobenzoin diacetate were found in any of the acetic acid decompositions listed in Table II, although all of these materials were stable to the reaction media. In addition, each of the products was found to be stable to the various media employed in the decompositions, and the product yields remained unchanged over a three day period.

Finally, the triazene decomposition using deuterated acetic acid gave vinyl acetates that exhibited essentially complete deuterium incorporation in the vinylic position.

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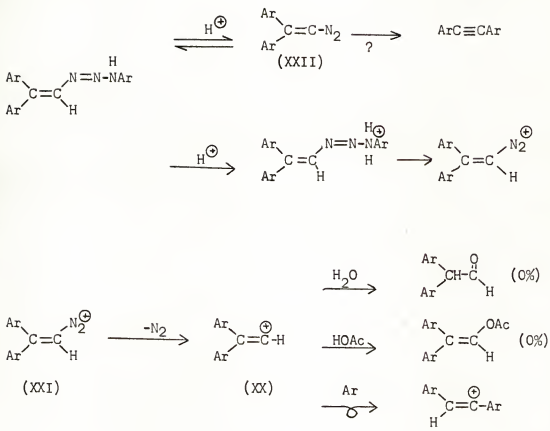
* Only one of the two acetates was isolated in pure form. Its properties showed that it had the same structure as the major vinyl acetate obtained from the reaction of desoxybenzoin and potassium acetate in acetic anhydride. TLC, preparative GLC, fractional crystallization and preferential isomer formation by changing the synthetic conditions failed to cleanly separate desoxybenzoin from the second isomer. GLC of the mixture, however, showed only two components. The IR spectrum and the NMR spectrum showed peaks expected for desoxybenzoin and quantitative GLC of the crude reaction mixture before and after hydrolysis showed that the amount of desoxybenzoin had increased at the expense of the unknown acetate.

Although the stereochemistry of neither isomer can be unequivocally assigned, both the ultraviolet (UV) and the NMR spectra support the assignment of the trans configuration to the major acetate formed in the reaction of desoxybenzoin and potassium acetate and the assignment of the cis configuration to the minor acetate that could not be separated from desoxybenzoin. Thus, the former (XIX) shows a UV maximum at 298 mμ., and the latter mixture shows no absorption above 281 mμ. The NMR spectrum of the proposed trans isomer shows a vinyl proton at 3.32τ, and the cis isomer exhibits the vinyl proton at 3.55τ. These properties are consistent with previous assignments made on model compounds (19).

The reactions outlined in Scheme J are suggested to explain these results. At the outset, it should be noted that the addition-elimination mechanism (Scheme G) is excluded for several reasons. First, the total absence of non-phenyl rearranged products is a strong argument against addition-elimination since it would require phenyl migration to the exclusion of acetate rearrangement. Second, the absence of diacetates or hydroxyacetates also argues against addition-elimination. Third, the formation of diphenylacetylene cannot be accommodated by this addition-elimination mechanism since the vinyl acetates and desoxybenzoin were independantly shown to be stable to the reaction conditions.

Scheme J includes the open vinyl cation, although the complete absence of products that would arise from the attack of a nucleophile of this cation, as well as the anticipated instability of the cation (XX) due to the absence of stabilizing substituent groups may suggest the possible involvement of the adjacent phenyl during the loss of nitrogen leading directly to the rearranged cation. The very rapid phenyl rearrangement of the open vinyl cation to the phenyl stabilized cation accomodates the experimental results equally well. This scheme differs from the general vinyl cation mechanism (Scheme G) in two essential features.

First an equilibrium between the vinyl diazonium ion (XXI) and the diazoalkene (XXII) is proposed to explain the total incorporation of deuterium into the vinyl position of cis and trans-1,2-diphenylvinyl acetate, since stability experiments excluded the incorporation of deuterium by the acetates after they had been formed. The equilibrium also served as a convenient explanation for the high percentage of



(Scheme J)

diphenylacetylene that was found in media that had low concentrations of base available to abstract a proton from the vinyl cation intermediate (11).

The second modification of the original vinyl cation mechanism that has been incorporated into Scheme J is the suggestion that the vinyl cation reacts with aniline as well as acetic acid. This modification was incorporated to explain the moderate yields of desoxybenzoin that were found in reactions despite rigorous attempts to exclude moisture. Thus, the aniline could compete with the acetic acid and lead to a protonated anil (XXIII), which could be hydrolyzed during the work-up to give the observed desoxybenzoin.*

The decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene under varying acetate concentrations, summarized in Table II, are quite consistant with Scheme J.

Compare the yields of products when the decomposition is run in acetic acid and the decomposition in the presence of added acetate (Reactions 1 and 4). In the presence of added acetate, more diphenylacetylene is formed and more 1,2-diphenyl acetate is also formed at the expense of desoxybenzoin. Both media are rich in nucleophiles but the acetate ion in potassium acetate is a much better nucleophile than acetic acid and more 1,2-diphenylvinyl acetate is formed. However, this better nucleophile is also more able to abstract a proton from the vinyl cation and the yield of diphenylacetylene is also increased. Further,

* Somewhat similar explanations have been used to explain products of this type found in anhydrous media (12c).

TABLE II

DECOMPOSITION OF 1-(2,2-DIPHENYLETHENYL)-3-PHENYL-1-TRIAZENE WITH VARIED ACETATE ION CONCENTRATION

Decomposition medium (a,b)	Relative yield diphenyl acetylene (XVI) (%yield)	Relative yield desoxybenzoin (XVII) (%yield)	Relative yield cis-1,2-diphenylvinyl acetate (XVIII) (%yield)	Relative yield trans-1,2-diphenylvinyl acetate (XIX) (%yield)
1) 7 ml. acetic acid	58 (56)	33.4 (32.3)	7.45 (7.2)	1.45 (1.4)
2) 2 mol. eq. acetic acid, 7 ml. benzene	64 (64)	35 (35)	trace	0
3) 1 mol. eq. acetic acid, 7 ml. benzene	77 (72.4)	23 (22.0)	0	0
4) 10 mol. eq. potassium acetate, 7 ml. acetic acid	67 (65.5)	17 (16.5)	12.5 (12.2)	3.4 (3.4)
5) 5.5 ml. acetic acid, 2.0 ml. acetic anhydride	59 (59)	21 (21)	12 (12.5)	8 (8.0)
6) 6 ml. acetic acid 1 ml. water	56 (53.0)	34 (32.5)	10 (9.5)	trace
7) 5.5 ml. deuterated acetic acid, 2.0 ml. acetic anhydride	59 (58)	20 (20)	13 (12.6)	8 (8.1)

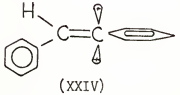
a. The following were submitted to the various media used in the decompositions and found to be stable: diphenylacetylene, desoxybenzoin, hydrobenzoin diacetate, diphenyl acetaldehyde, 2,2-diphenylvinyl acetate and 1,2-diphenylvinyl acetate cis and trans.

b. All reactions were run at room temperature on 0.5000 g. of triazene. The yields were obtained using GLC with methyl cinnamate as an internal standard. It was assumed that the flame ionization detector response was directly proportional to the concentration of the product in grams (20). A reproducible accuracy of ± 1 percent was assured by duplicate experiments and calibration curves.

the low relative concentration of aniline in the medium precludes the capture of the cation by aniline and lowers the amount of (XXIII) which can by hydrolysis lead to desoxybenzoin. Consider (Reactions 1,2 and 3) where the acetic acid concentration is decreased. The drastic decrease in acetic acid concentration could cause an increase in the amount of diphenylacetylene by shifting the diazonium-diazo equilibrium to favor the formation of diphenylacetylene. The decrease in the ratio of vinyl acetate to desoxybenzoin in low acetic acid concentration is also accommodated since the aniline concentration has not been lowered and can still intercept the vinyl cation at low acetic acid concentrations, leading to desoxybenzoin by eventual hydrolysis of the anil (XXIII).

It is also most interesting that the principal vinyl acetate produced is consistantly the one in which it is believed that the two phenyls are cis with respect to each other. This experimental result also agrees well with Scheme J. The attack on the vinyl cation (XXIV) by solvent must occur in the plane of the geminal phenyl and hydrogen and the direction of approach that would lead to the trans isomer would be hindered by the phenyl group. Thus, the attack of the solvent from the less hindered side gives the cis acetate.

The results of the decomposition of the diphenyl triazene with varying acetate concentrations led to attempts to intercept three of the postulated intermediates. The acidic decomposition in the presence



(XXIV)

of dimethyl fumarate, cyclohexene or α-naphthol failed to intercept the diazoalkene, the vinylidene or the vinyl diazonium ion. The control reactions (Table III, Reactions 1,2,3 and 4) where no trapping agent was added led to approximately the same yields of products as the remaining reactions which were run in the presence of the trapping agents. Thus, the diphenyl diazonium ion (XXI), the diazoalkene (XXII) and the vinylidene were not intercepted under the experimental conditions employed here. Curtin (7) has reported similar failure in his attempts to intercept the diphenyl diazonium ion and the vinylidene in the nitrosation of diphenylvinylamine.

Since the vinylidene could conceivably result from the decomposition of the parent triazene with base, the triazene was treated with base under a variety of conditions summarized in Table III. Aqueous glycine did not liberate nitrogen from the triazene at room temperature. Lithium ethoxide in hot ethanol did not liberate nitrogen from the triazene and no gas was evolved when an ethereal solution of the triazene was treated with butyllithium at at room temperature. The base stability of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene made the interception of the vinylidene impossible under the basic conditions employed in this study.

All of the data gathered throughout this study are remarkably consistant with the vinyl cation mechanism, whether each triazene is considered individually or in combination with the data gathered on the other triazenes that were part of this study. The addition-elimination mechanism (Scheme G) can also explain some of the results if the triazenes are considered on an individual basis, but if the data

gathered on all of the triazenes are considered together, the addition-elimination mechanism as the exclusive pathway to products becomes unlikely.

TABLE III

ATTEMPTED INTERCEPTION OF THE PRECURSORS OF THE 1,2-DIPHENYLVINYL CATION (a)

Decomposition medium	Percent yield diphenylacetylene	Percent yield benzophenone (b)
1) 15 ml. benzene, 1 mol. eq. acetic acid	85	0
2) 15 ml. benzene, 1 mol. eq. acetic acid, 1 g. dimethyl fumarate	84	0
15 ml. cyclohexene, 1 mol. eq. acetic acid	88	0
2) 5 ml. heptane (c)	62	28
5 ml. heptane, (c) 1 g. dimethyl fumarate	63	28
3) 10 ml. cyclohexane 354 hv	21	74
10 ml. cyclohexene 354 hv	21	71
4) 7 ml. tetrahydrofuran, 1 mol. eq. 40 percent aq. fluoboric acid (d)	67	0
7 ml. tetrahydrofuran, 1 mol. eq. 40 percent aq. fluoboric acid, 2 mol. eq. naphthol (d)	64	0
1 mol. eq. glycine, 7 ml. water (e)	0	0
2 mol. eq. lithium ethoxide, 7 ml. ethanol (e)	0	0
1 mol. eq. butyllithium, 7 ml. ether (e)	0	0

TABLE III (continued)

a. All reactions were run on 0.2000 g. of triazene. The yields were determined using GLC. All reactions were run at room temperature unless otherwise stated.

b. Thermal and photolytic decomposition led to benzophenone, identified by IR comparison to an authentic sample.

c. This reaction was run at the refluxing temperature of the solvent.

d. These reactions also gave 28 percent desoxybenzoin, and were run at 0° and at room temperature.

e. No gas evolution observed in twenty-four hours.

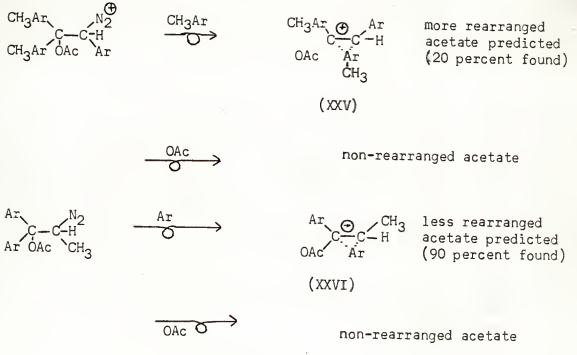
VI. A DISCUSSION OF THE ADDITION-ELIMINATION MECHANISM IN THE ACID DECOMPOSITION OF THE VINYL TRIAZENES

If the decompositions of the three triazenes, 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene (VIII), 1-(2,2-diphenyl-methyl-ethenyl)-3-phenyl-1-triazene (IX) and 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene (X) in the presence of acetic acid proceeded exclusively by the addition of acetic acid to the diazonium ion followed by rearrangement and elimination (Scheme G), there are three common types of rationalization that could be invoked to explain the products found.

First, if the total reason for preferential migration is due to the relative stabilities of the transition states in some type of bridged "onium" compound (VIII), should give more phenyl migration than (IX) (Scheme K).

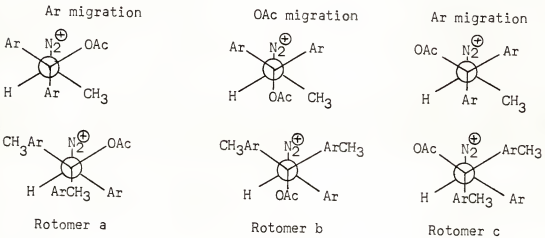
The decomposition of the di-p-tolyl triazene (VIII) with acetic acid led to only 20 percent rearranged product, but the decomposition of the diphenyl methyl triazene (IX) led to more than 90 percent rearranged acetate.

Second, if the total reason for preferential rearrangement is due to the rotational conformation of the diazonium ion, the di-p-tolyl-phenyl triazene should give more non-rearranged acetate than the diazonium ion from the diphenyl methyl triazene since the most stable rotomer is the one which should lead to phenyl migration (Scheme L) and



(Scheme K)

the phenyl migrating rotomer should be even more prefered in the diazonium ion from the di-p-tolyl triazene (Scheme L) (21).



(Scheme L)

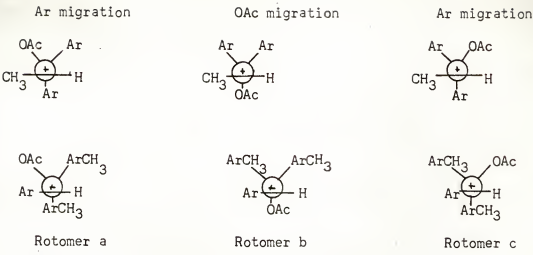
Since methyl is smaller than phenyl, the population of molecules in the rotomer "c" conformation should be less in the di-p-tolyl system than in the diphenyl methyl system. Since rotomer

"c" is one which should lead to rearranged acetate by phenyl migration, the decomposition of the diphenyl methyl triazene with acetic acid should give more rearranged acetate than would be found in the decomposition of the di-p-tolyl phenyl triazene. This prediction is experimentally verified. The diphenyl methyl system gives 90 percent rearranged product and the di-p-tolyl phenyl system gives only 20 percent rearranged product.

However, even if it assumed that rotomer "c" is too high energetically to be significantly populated, the maximum amount of acetate that can migrate is less than 50 percent since the most stable rotomer is rotomer "a" which predicts phenyl migration leading to rearranged acetate. This is not verified experimentally. The diazonium ion from the di-p-tolyl triazene could not lead to 80 percent non-rearranged acetate through the less stable "b" rotomer. A consideration of the rotomers of the diazonium ions resulting from the addition-elimination mechanism does not agree with the experimental evidence gathered.

Third, if the total reason for preferential migration is the rotational conformation of the cation after the loss of nitrogen, preceding rearrangement, the di-p-tolylphenylvinyl cation from the acetic acid decomposition of the di-p-tolyl phenyl triazene (VIII) should give more rearranged acetate than the diphenylmethylvinyl cation from the decomposition of the diphenyl methyl triazene (Scheme M) (21).

This prediction follows from a study of the rotomers. Since a phenyl is larger than a methyl group, it follows that the rotomer "a" conformation leading to rearranged acetate should contribute more to the reaction in the case of the decomposition of the di-p-tolyl triazene



(Scheme M)

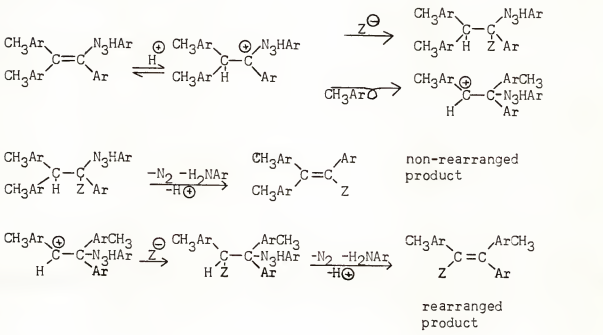
than in the case of the decomposition of the diphenyl-methyl triazene. The predicted result is that more rearranged acetate should be found in the decomposition of the di-p-tolyl triazene. This is not experimentally verified. The decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene led to 20 percent rearranged acetate but the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene led to 90 percent rearranged acetate.

The three common rationale for the products, if the addition-elimination mechanism (Scheme G) is the sole pathway to products, cannot explain the results found in the acetic acid decompositions of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene and 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene.

Finally, the decompositions of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene gave diphenylacetylene as the major product and the remaining products were all phenyl "migrated". Since the probable products from the nucleophilic attack on the diazonium ion intermediate

do not lead to diphenylacetylene under reaction conditions, the high yields of diphenylacetylene are not explained by the addition-elimination mechanism, and exclusive phenyl migration is not evident by considering rotomers. In the same decomposition the preferential formation of cis-1,2-diphenylvinyl acetate rather than trans-1,2-diphenylvinyl acetate is likewise unexplained by the addition-elimination mechanism (Scheme G) as the sole pathway to products.

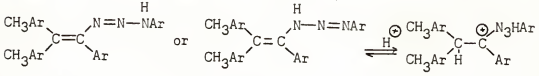
The second possible addition-elimination mechanistic pathway to products, also considered by Curtin (7) is summarized below (Scheme N).



(Scheme N)

Ar the outset, it should be noted that because of the proposed competition between nucleophilic attack on a non-rearranged cation and rearrangement, a discussion of the relative amounts of rearranged and non-rearranged products cannot distinguish between this addition-elimination mechanism (Scheme N) and a similar competition in the

vinyl cation mechanism. Furthermore, the rearrangement to a less stable cation to account for the 20 percent of rearranged acetate found in the acetic acid decomposition of the di-p-tolyl triazene (VIII) does not rule out the pathway. Similar protonation (Scheme O) is well known in the "enamine" system (22).

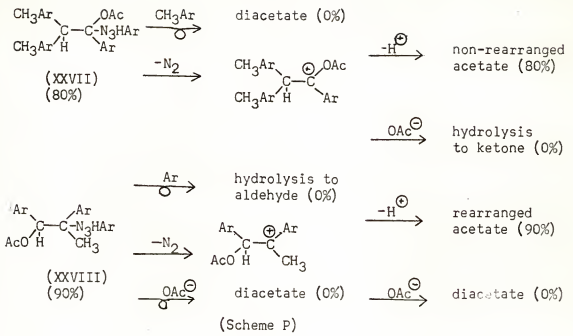


(Scheme O)

This mechanism might explain some of the results of the study but, as the sole pathway to products, if fails to justify several findings.

First, consider the results of the sulfuric acid decomposition of the triphenyl triazene (I) which indicate that nitrogen has been evolved to give an intermediate that could react with acetic acid to give the observed triphenylvinyl acetate. The addition-elimination mechanism (Scheme N) does not readily explain the results of the sulfuric acid decomposition of this triazene (13).

Next, consider the decomposition of the di-p-tolyl triazene (VIII) in glacial acetic acid to give 80 percent of non-rearranged acetate and the glacial acetic acid decomposition of the diphenyl methyl triazene (IX) where 90 percent of the acetate product was rearranged. If the addition-elimination mechanism (Scheme N) were the sole pathway to products, it follows that the major pathway to products is the decomposition of two intermediates (XXVII, XXVIII) respectively to give only two products (Scheme P).

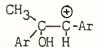


(Scheme P)

Since the diazotization of related amino alcohols in acetic acid (11,23), the solvolyses of related bromohydrins (23) and the acetolyses of related brosylates (24,25) all proceed with varying degrees of participation and rearrangement to give a wide variety of products, it is not obvious that the decomposition of (XXVII) and (XXVIII) should proceed to a single product with no partipation or rearrangement.

More specifically, Collins and co-workers (23b) have postulated that the deamination of D- and L-erythro-1-amino-1,2-diphenyl propanol-2 and the deamination of erythro and threo-1-amino-1-phenyl-2-p-tolyl-2-propanol proceeded through (XXIX) and (XXX) with either participation or equilibrating cations to give several ketones and Felkin (23c) has shown that the deamination of 1,2-diphenyl-2-amino ethanol proceeded through (XXXI) to give a mixture of glycol and epoxide.

(XXIX)

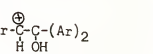


(XXX)

(XXXI)

In addition, Winstein (24) has shown that the acetolysis of 2,2-diphenyl-1-methoxyethyl brosylate proceeded through (XXXII) to give a phenyl ketone after attack by acetic acid, followed by hydrolysis; and Lane and Walters (25) have shown that the hydrolysis of triphenylethyl bromohydrin proceeded through (XXXIII) to give mixtures of phenyl benzhydryl ketone and triphenylethyleneglycol.

(XXXII)



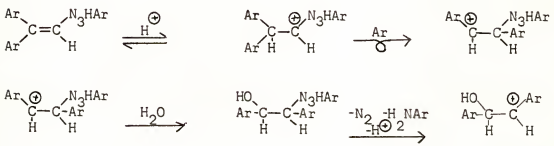
(XXXIII)

In light of the work of Lane and Walters (25), the absence of diacetate and ketone in the acetic acid decomposition of the di-tolyl triazene is not explained by the addition-elimination mechanism. The absence of diacetate in the acetic acid decomposition of the diphenyl methyl triazene is also obscure if the addition-elimination mechanism (Scheme N) is the sole pathway to products in view of the work of Collins (23b).

Consider the experimental results in the acetic acid decompositions of the diphenyl triazene (X), summarized in Table II. If the addition-elimination mechanism were the sole pathway to products, it follows that one source of desoxybenzoin is the decomposition of (XXXIV) (Scheme Q).

Since previously cited work of Felkin (23c) has shown that (XXXI), identical to (XXXIV), gave glycol and epoxide and Brewer and Zincke (23e) have shown that the acid decomposition of hydrobenzoin gave diphenylacetaldehyde, (XXXI) a probable intermediate, the absence of diphenylacetaldehyde, glycol and diacetate in the decomposition of the diphenyl

triazene (X) are not explained by the addition-elimination mechanism (Scheme N) as the sole pathway to products.



(XXXIV)

(Scheme Q)

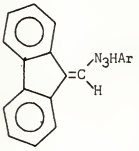
Finally, this type of mechanism was originally postulated by Curtin (7) to account for the presence of approximately 30 percent of non-phenyl "migrated" product, diphenylchloroacetaldehyde, in the nitrosation of 2,2-diphenylvinyl amine. By contrast, all of the acetic acid decompositions of the diphenyl triazene gave exclusively phenyl "migrated" products.

Although it is possible that a fortuitous set of circumstances have intervened and the mass of experimental data could be explained by a complex set of multiple mechanisms, the data collected are most simply rationalized with a vinyl cation mechanism.

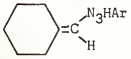
Therefore, the experimental evidence led to the conclusion that the vinyl cation is a probable intermediate in the acid decompositions of 1-(triphenylethenyl)-3-phenyl-1-triazene (I), 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene (VIII), 1-(2,2-diphenyl-methylethenyl)-

3-phenyl-1-triazene (IX), and 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene (X).*

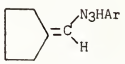
* During the course of this research the syntheses of the following triazenes were unsuccessfully attempted.



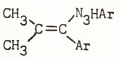
(XXXV)



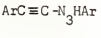
(XXXVI)



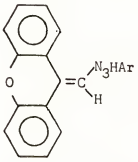
(XXXVII)



(XXXVIII)



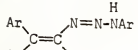
(XXXIX)



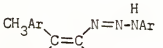
(XXXX)

VII. SUMMARY

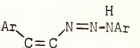
The syntheses of 1-(triphenylethenyl)-3-phenyl-1-triazene (I), 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene (VIII), 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene (IX) and 1-(2,2-diphenyl-ethenyl)-3-phenyl-1-triazene (X) are reported.



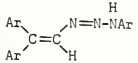
(I)



(VIII)



(IX)



(X)

When treated with acid at room temperature, all of the triazenes liberated nitrogen.

The triphenyl triazene (I) was decomposed with a wide variety of acids, leading to good yields of triphenylvinyl acetate, tosylate, and phenolate. In the presence of aqueous acid, phenyl benzhydryl ketone was formed. When the triazene (I) was decomposed with cold sulfuric acid and added to ice, phenyl benzhydryl ketone was formed. If the sulfuric acid mixture was added to a cold slush of glacial acetic acid, triphenylvinyl acetate and phenyl benzhydryl ketone were formed.

The acetic acid decomposition of the di-tolylvinyl triazene (VIII) gave 1,2-di-tolyl acetate and 2,2-di-tolyl acetate in 20 and 80 percent yield respectively. Diphenyl-methyl triazene (IX), when treated

with acetic acid, yielded 1,2-diphenylvinyl acetate and 2,2-diphenylvinyl acetate in the ratio of 9:1 and small amounts of α-phenylpropiophenone.

The decomposition of the diphenylvinyl triazene (X) was carried out in media with varied acetate concentration. Diphenylacetylene was the major product. Lesser amounts of desoxybenzoin and both cis and trans-1,2-diphenylvinyl acetate were found.

Mechanistically the products suggest a vinyl cation intermediate.

VIII. EXPERIMENTAL

General.-- A wilkins Aerograph Gas Chromatograph Model 600-B equipped with a 1/8 in. x 5 ft. copper column packed with 20 percent SE-30 on 60/80 mesh Gas Chrom. Z. was used for routine GLC analyses.* Methyl cinnamate was used as an analytical internal standard.

A Perkin Elmer Infracord Spectrophotometer was used for IR analyses.

NMR spectra were determined with a Varian A-60 using deuterated chloroform as the solvent and tetramethylsilane as an internal standard.

UV analyses were made on a Cary-14 Recording Spectrophotometer.

TLC separations were made on silica gel HF-254 substrate using ether-pentane mixtures for development.

Elemental analyses were made by Galbraith Laboratories, Knoxville, Tennessee.

All triazenes were stored under nitrogen to obtain maximum shelf life.

All compounds for which no preparative techniques are listed were obtained commercially.

All melting points and boiling points are uncorrected.

No attempts were made to maximize yields.

Uniformly successful results were obtained in the preparation of

* Compounds with an empirical formula of C_{20} or larger were held on the column and were more conveniently handled using TLC. GLC accuracy was assured by duplicate experiments and calibration curves.

vinylic Grignard intermediates if the following general precautions were taken:

1. Anhydrous ether was removed from septum sealed cans using nitrogen pressure and degassed prior to use.
2. No lubrication was used on ground glass joints.
3. The assembled apparatus and magnesium were flamed under a stream of nitrogen.
4. All vinyl bromides were rigorously purified immediately prior to use.
5. The magnetic stirring bars were boiled in toluene prior to use.
6. Liquid reagents were added through septums. Solids were added under nitrogen.

Preparation of bromo-2,2-diphenylethylene.--Bromo-2,2-diphenylethylene was prepared by the method of Hepp (26) using 1,1-diphenylethylene (26) and bromine. Dehydrohalogenation of the dibromide was accomplished by heating the solid for three hours on a steam bath using a rotary evaporator. Vacuum distillation at 134-6°/ 2mm. afforded the product, m.p. 49° (83% yield) (lit. m.p. 50°).

Preparation of bromo-triphenylethylene.--Bromotriphenylethylene was prepared in excellent yield from triphenylethylene (27) using the method of Koelsch (28). The product, m.p. 113-114°, was crystallized from acetic acid (94% yield) (lit. m.p. 114-115.5°).

Preparation of bromo-phenyl-(2,2-di-p-tolyl)-ethylene.--An adaptation of the preparation of triphenylethylene (27) using di-p-tolyl ketone (29), gave the substituted ethylene in good yield. The method of Koelsch (28) was used to give the bromide, m.p. 131-3° (81% yield), after crystallization from ethanol (lit. m.p. 132-3°).

Preparation of bromo-methyl-(2,2-diphenylethylene).--Methyl-2,2-diphenylethylene was prepared by an adaptation of the method of Adkins and Zartman (27) using ethylmagnesium bromide and benzophenone. The resulting ethylene, b.p. 110°/ 0.5 mm., (lit. b.p. 149°/ 11 mm.) (30), was brominated with bromine in cold pentane. The solvent was removed with a rotary evaporator and replaced with glacial acetic acid. The crude dibromide was dehydrobrominated by refluxing the resulting solution for several hours. The reaction mixture was poured over ice and extracted into ether. The ether layer was washed with water, sodium bicarbonate and finally with water till neutral. After drying over magnesium sulfate, the bromide was distilled, b.p. 155-7°/ 1 mm. (81% yield), and obtained as a slushy pale yellow oil (30) (lit. m.p. 48-9°). Both the IR and UV spectra were compatible with the proposed structure and GLC showed the compound to be pure.

Preparation of phenyl azide.--Phenyl azide was prepared from phenyl hydrazine using the method of Lindsay and Allen (31). The product was obtained as a pale yellow oil (67% yield). It was more convenient to carry out the final distillation at pressures under 1 mm. and enclose the receiver in dry ice. At this lower pressure phenyl azide distilled at room temperature and solidified in the receiver.

Preparation of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene (X).--A dry three neck flask fitted with a condenser and a septum sealed dropping funnel was swept with nitrogen and charged with 0.9728 g. (0.040 moles) of magnesium turnings and a stirring bar.* To this was added 100 ml. of

* For a summary of the general vinyl Grignard techniques used see the first paragraphs of VIII. EXPERIMENTAL. For lead references on triazenes see (12).

dry ether and a crystal of iodine. A solution of 10.368 g. (0.040 moles) of bromo-2,2-diphenylethylene in 50 ml. of dry ether was added dropwise. The mixture was brought to reflux with stirring. After forty-eight hours the magnesium had been consumed. The reaction mixture was cooled to room temperature and 4.760 g. (0.040 moles) of phenyl azide in 50 ml. of dry ether was slowly added to the limpid yellow solution. The mixture turned deep red. The solution was stirred for three hours at room temperature and 50 ml. of stock ammonium chloride-ammonia solution was added slowly with cooling. (This stock solution was made from 10 g. of ammonium chloride and 33 ml. of ammonium hydroxide diluted with water to 100 ml. total volume.) A yellow precipitate formed which slowly dissolved in the ether layer. The organic layer was separated and dried over magnesium sulfate. The trace amounts of ammonia dissolved in the ether layer seemed to stabilize the crude triazene. The solvent was evaporated with a stream of nitrogen leaving a dark oil. Approximately 20 ml. of pentane was added and the mixture was refrigerated for several days. The triazene, which separated as a yellow solid, was powdered. The powder was filtered and washed with small amounts of cold pentane. Drying of the triazene under vacuum afforded 7.31 g. (60.8% yield) of pale yellow powder, m.p. 117-8° with effervescence. Since the melting point of the triazene varied from batch to batch, TLC and nitrogen evolution were used as purity criteria. Thus, if a sample of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene gave greater than 95 percent of the theoretical nitrogen when treated with acid, and if TLC showed trace amounts of 1,1,4,4-tetraphenyl-1,3-butadiene as the sole contaminant, it was used. Recrystallization from petroleum ether afforded a product of no higher purity and resulted in large product loss.

Chromatography on silica gel and other typical solid purification techniques decomposed the product.* The major contaminant in the preparation was an uncharacterized red oil which degassed when treated with acid and possibly contained the isomeric 3-(2,2-diphenylethenyl)-1-phenyl-1-triazene. Small amounts of 1,1,4,4-tetraphenyl-1,3-butadiene, m.p. 200° (32), diphenylacetylene, m.p. 60° (33), and aniline were also found. The IR spectrum of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene exhibited peaks at 3.0, 3.3 and 6.3 μ. The UV spectrum exhibited a broad maximum at 370 mμ. The NMR spectrum exhibited a sharp singlet at 2.35τ and a multiplet at 2.75τ .

Anal. Calcd. for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.21; h, 5.80; N, 13.82.

Ozonolysis of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene.--A 0.050 g. (0.000167 moles) sample of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene was dissolved in 10 ml. of ethyl acetate, cooled to 0° and treated with ozone for fifteen minutes. The ethyl acetate was removed with a rotary evaporator and the crude ozonide was treated with 2 ml. of water, a trace of zinc dust and several drops of acetic acid. The mixture was refluxed with stirring for two hours. The organic material was extracted into ether and washed well with bicarbonate solution and water. After drying over magnesium sulfate, the ether was removed with a stream of nitrogen. The 0.0281 g. of solid had a GLC retention time that was

* The other triazenes were used when they gave a single spot on TLC and evolved greater than 95 percent of the theoretical nitrogen when treated with acid (23d).

identical to that of authentic benzophenone. No peak was present with a retention time identical to that of benzaldehyde. The IR spectra of the ozone reaction product and authentic benzophenone were super imposible.

Preparation of 1-(triphenylethenyl)-3-phenyl-1-triazene (I).--This triazene was prepared by the method described earlier for the preparation of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. The time required for the consumption of the magnesium was three hours. Crystallization from pentane afforded yellow crystals, m.p. 102-3° with effervescence (59% yield).* The IR spectrum exhibited peaks at 3.0, 3.3 and 6.3 μ. The NMR spectrum exhibited a multiplet at 2.9τ .

Anal. Calcd. for $C_{26}H_{21}N_3$: C, 83.17; H, 5.64; N, 11.19. Found: C, 82.99; H, 5.51; N, 11.25.

Ozonolysis of 1-(triphenylethenyl)-3-phenyl-1-triazene.--The ozonolysis was carried out as previously described. A high yield of benzophenone was found. The ozonolysis product had an IR spectrum that was superimposible on a spectrum of authentic sample.

Preparation of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene (VIII).--This triazene was prepared by the method described earlier for the preparation of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. Total magnesium consumption required several days. After washing with pentane, the product was obtained as a yellow solid, m.p. 67° with effervescence (62% yield).* The IR spectrum exhibited peaks at 3.0, 3.3, 3.5 and 6.25 μ.

* TLC and nitrogen evolution were used as purity criteria rather than melting point (23d).

Anal. Calcd. for $C_{28}H_{25}N_3$: C, 83.34; H, 6.24; N, 10.41. Found: C, 83.09; H, 6.36; N, 10.57.

Ozonolysis of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene.-- The ozonolysis of this triazene was carried out as previously described. The resulting solid product had an IR spectrum that was superimposible on a spectrum of authentic di-p-tolyl ketone. GLC showed a peak with retention time identical to that of di-p-tolyl ketone, but no peak was present that had a retention identical to that of p-methylbenzophenone.

Preparation of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene (IX).-- The method described earlier for the preparation of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene was adapted for the preparation of this triazene. Crystallization from pentane, which took nearly a week, gave the product, m.p. 86-7° with effervescence (10.5% yield).* Although the heat generated by the IR source had a tendency to decompose the triazene, the IR spectrum exhibited peaks at 3.0, 3.3 and 6.25 μ. This triazene was too unstable for elemental analysis, but compelling evidence for the proposed structure was found. First, the triazene evolved 97 percent of the theoretical nitrogen when treated with acid. Second, the IR spectrum was compatible with the proposed structure. Third, the results of the decomposition of the triazene with acetic acid, namely the production of vinyl acetates and acetanilide, strongly suggested the structure.

Ozonolysis of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene.-- The ozonolysis of this triazene was carried out as previously described.

* TLC and nitrogen evolution were used as purity criteria rather than melting point (23d).

The resulting solid product had an IR spectrum that was superimposible on a spectrum of authentic benzophenone. GLC showed a peak with retention time identical to that of benzophenone, but no peak was present that had a retention time identical to that of acetophenone.

Preparation of diphenylacetylene.--Diphenylacetylene was prepared by the method of Smith and Falkof (34). Several crystallizations from alcohol produced the product, m.p. 60° (lit. m.p. 60-1°).

Preparation of 1,1,4,4-tetraphenyl-1,3-butadiene.--The preparation of 1,1,4,4-tetraphenyl-1,3-butadiene was accomplished by treating 3.0 g. of bromo-2,2-diphenylethylene with equimolar magnesium and a crystal of iodine in ether as described for the preparation of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. After the magnesium had been consumed, the ether was removed with a stream of nitrogen and 25 ml. of toluene was added. The mixture was brought to reflux for three hours and poured into water. The layers were separated and the organic layer was dried over magnesium sulfate. The toluene was concentrated to approximately one-half volume and cooled. The preparation gave 1.3 g. of white solid, m.p. 200°, after crystallization from petroleum ether (32) (lit. m.p. 203°). The IR spectrum was compatible with the proposed structure. The NMR spectrum showed a multiplet at 2.6τ and a singlet at 3.21τ .

Preparation of sodium p-toluenesulfinate and p-toluenesulfinic acid.--The procedure of Whitmore and Hamilton (35) was used to prepare sodium p-toluenesulfinate from p-toluenesulfonyl chloride. P-toluenesulfinic acid was prepared by acidifying an aqueous solution of the sodium salt as suggested by these same authors.

Preparation of di-p-tolyl ketone.--Di-p-tolyl ketone was prepared by an adaptation of the method of Marvel and Sperry (29) using toluene, carbon tetrachloride and aluminum trichloride. After hydrolysis of the dichloride, the crude reaction mixture was extracted into ether, washed thoroughly with water and dried over magnesium sulfate. GLC showed three components. The mixture was concentrated to a slushy solid with a rotary evaporator and filtered through a sintered glass funnel. A white solid remained which was washed well with pentane to eliminate the last traces of oil. Recrystallization from alcohol afforded the product, m.p. 93-4° (84% yield) (36) (lit. m.p. 95°). GLC showed the purity of the synthesized di-p-tolyl ketone to be greater than 97 percent. Di-p-tolyl ketone was also prepared in good yield using p-toluic acid, toluene and aluminum trichloride, an adaptation of the method of Allen and Barker (37).

Preparation of p-methylbenzophenone.--p-Methylbenzophenone was prepared by an adaptation of the method of Allen and Barker (37) using p-toluic acid, benzene and aluminum trichloride. The product was distilled, b.p. 115-20°/ 0.5 mm., and obtained as an oil which solidified, m.p. 57° (75% yield) (36) (lit. m.p. 60°).

Preparation of desoxybenzoin.--Desoxybenzoin was prepared from phenylacetic acid using the method of Allen and Barker (37). The product was distilled, b.p. 120°/ 0.25 mm., and obtained as a colorless oil which solidified, m.p. 55°, and was used directly without further purification. The NMR spectrum of desoxybenzoin exhibited peaks at 2.7τ, aromatic multiplet, and a singlet at 5.78τ.

Preparation of phenyl benzhydryl ketone.--Phenyl benzhydryl ketone was

prepared by the method of Bonner and Collins (38) using diphenylacetic acid and diphenylcadmium. Phenyl benzhydryl ketone, m.p. 134-5° (71% yield), was obtained after crystallization from alcohol (lit. m.p. 136-136.5°).

Preparation of cis and trans-1,2-diphenylvinyl acetate (19).--*Desoxybenzoin, 14.0 g., was added portionwise with stirring to a warm solution of 28.0 g. of dry potassium acetate in 50 ml. of acetic anhydride. The mixture was brought to reflux with stirring for three hours, cooled, and poured into ice water. The resulting oily solid was taken up in ether and washed with water till neutral. The ether layer was dried over magnesium sulfate and, following filtration through a bed of decolorizing carbon, was analysed by GLC. Three components were present in a ratio of 20:3:1. Upon evaporation of the ether layer to about 50 ml. total volume, the major component crystallized in fine white needles. Alternate crystallizations from ethanol and petroleum ether, b.p. 65-110°, gave pure trans isomer (XIX), m.p. 101° (78% yield) (lit. m.p. 101°). Further concentration of the mother liquors afforded a second crop of the trans acetate. The IR spectrum of trans-1,2-diphenylvinyl acetate exhibited peaks at 5.7, 6.2 and 8.3-8.5 μ. The UV spectrum of the trans isomer exhibited a broad maximum centered at 298 mμ. The NMR spectrum of the trans isomer showed a multiplet at 2.6τ and two singlets at 3.32τ and 7.76τ in the ratio of 1:3. The mother liquors were again analysed by

* Although the rigorous identification of the cis and trans isomers of 1,2-diphenylvinyl acetate is not claimed, tentative isomer identification is suggested by the evidence gathered. Therefore, throughout this work, the major vinyl acetate obtained by the method of Barnes (39) will be referred to as trans-1,2-diphenylvinyl acetate (XIX).

GLC. Three components were present in the ratio of 1:1:1. One of the three components had a GLC retention time identical to that of trans isomer. A second component had a retention time identical to that of desoxybenzoin. Further, an IR spectrum of the mixture exhibited all of the peaks present in an IR spectrum of authentic desoxybenzoin. The IR spectrum also exhibited peaks at 5.7, 6.2 and 8.3-8.5 μ. The literature suggests that little difference is to be expected in the IR spectra of the two isomers (19a). The crude mixture was further enriched by fractional crystallization and subjected to UV analysis. No absorption was observed above 281 mμ. GLC showed only trace amounts of the trans isomer to be present, but the desoxybenzoin was still present as a major contaminant. The NMR spectrum exhibited a multiplet at 2.6τ, a small singlet at 3.32τ (trace contamination by the trans isomer), a singlet at 3.55τ, a peak at 5.75τ (the benzylic hydrogens of desoxybenzoin) and multiple peaks from 7.70τ to 8.2τ (19b,c). The enriched mixture hydrolyzed to desoxybenzoin when treated with aqueous ethanolic hydrochloric acid. GLC showed that the amount of desoxybenzoin present after hydrolysis was greater than could have been obtained by the hydrolysis of the trans isomer known to be present in the mixture. Separation was attempted using chromatography on silica gel, preparative TLC, preparative GLC, and fractional crystallization with common solvents and solvent pairs. The reaction was attempted using acetyl chloride and trace amounts of sulfuric acid, acetyl chloride, zinc dust and acetyl chloride (19a), and hydration of diphenylacetylene with mercuric acetate (19d). Thus, the usual methods of isomer separation and preferential isomer formation by changing reaction conditions met with little

success and the cis isomer (XVIII) was never obtained pure.

Preparation of 2,2-diphenylvinyl acetate.--A sample of 2,2-diphenylvinyl acetate was synthesized by the method of Barnes (39) using diphenylacetaldehyde for comparison to the products of the decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. After the mixture had been extracted into ether and washed with water, it was dried over magnesium sulfate and filtered through a bed of decolorizing carbon. The solvent was removed with a rotary evaporator and the resulting oil was chromatographed over silica gel using ether-pentane eluent. An oil, which gradually solidified, was obtained. The 2,2-diphenylvinyl acetate was crystallized from alcohol and obtained as a white solid, m.p. 58-60° (40) (lit. m.p. 60°). The IR spectrum exhibited peaks at 5.7, 6.15 and 8.3 μ. The NMR spectrum exhibited no peaks in the 3.1-4.0τ region. The GLC retention time of 2,2-diphenylvinyl acetate was different from cis and trans-1,2-diphenylvinyl acetate.

Preparation of triphenylvinyl acetate.--Triphenylvinyl acetate was prepared by the method of Barnes (39). Phenyl benzhydryl ketone, 7.0 g., was refluxed for one hour with 14.0 g. of dry potassium acetate and 50 ml. of acetic anhydride. The mixture was cooled, poured into water, and extracted into ether. The organic layer was washed with water, dried over magnesium sulfate and concentrated with a stream of nitrogen to give a solid which was crystallized from petroleum ether, b.p. 65-110°. Triphenylvinyl acetate was obtained as a colorless crystalline solid, m.p. 104-5° (lit. m.p. 104°). The IR spectrum exhibited peaks at 3.3, 5.7, 6.1, 6.3 and 8.3 μ.

Preparation of triphenylethyleneglycol diacetate.--Triphenylethylene-

glycol diacetate (41) was prepared by treating triphenylethyleneglycol (42) with acetyl chloride. The product, crystallized first from alcohol then from benzene-petroleum ether, had a m.p. of 213-14°. Its NMR spectrum exhibited a phenyl multiplet at 2.9τ and peaks at 3.33τ and 8.1τ in a ratio of 1:6 respectively (lit. m.p. 213-14°).

Preparation of hydrobenzoin diacetate.--Hydrobenzoin diacetate (43) was prepared by treating hydrobenzoin (19a) with acetyl chloride. The product, m.p. 132-3° after crystallization from alcohol, had an NMR spectrum that exhibited a phenyl multiplet at 2.78τ , a peak at 3.9τ and a peak at 8.1τ . The ratio of peak areas was 10:2:6 respectively (lit. m.p. 134°).

Typical decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene with acetic acid.--A dry three neck flask was fitted with a gas burette, septum, stirring bar and a solid addition tube containing 0.5000 g. (0.000167 moles) of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. Seven ml. of dry acetic acid, prepared by distillation from acetic anhydride, was added and the stirrer was started. After equilibration, the solid addition tube was inverted. Gas evolution (34.4 ml.) was complete within two minutes. The mixture was evaporated to dryness at room temperature under vacuum and the resulting yellow solid was analysed for products.* Preparative TLC was used to isolate 1,1,4,4-tetraphenyl-1,3-butadiene and diphenylacetylene. Both were identical in melting point and had IR spectra that were superimposible on the spectra of authentic samples. Since there was a trace of 1,1,4,4-tetraphenyl-1,3-butadiene in the

* See Table II for a listing of conditions and yields of the various products.

starting triazene, the amount produced in the reaction was not determined. In addition, GLC showed peaks that had retention times identical to those of diphenylacetylene 56 percent, desoxybenzoin 32.3 percent, cis-1,2-diphenylvinyl acetate 7.2 percent, trans-1,2-diphenylvinyl acetate 1.4 percent and acetanilide. From preparative TLC a mixture of cis and trans-1,2-diphenylvinyl acetate and desoxybenzoin was isolated. The IR spectrum of this mixture was identical to the IR spectrum of an independently made mixture of authentic samples. Furthermore, an NMR spectrum of the three component mixture, isolated by preparative TLC exhibited peaks at 3.32, 3.55 and 5.74τ which is compatible with a mixture of desoxybenzoin and cis and trans-1,2-diphenylvinyl acetate. A sample of the reaction mixture was hydrolyzed with aqueous ethanolic hydrochloric acid. GLC of the hydrolysis product showed that the amount of desoxybenzoin present had increased at the expense of both vinyl acetates.*

Attempted interception of vinyl diazonium ion with ß-naphthol.--A three neck flask was fitted with a magnetic stirring bar, septum, gas burette and a solid addition tube containing 0.5000 g. of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. Seven ml. of tetrahydrofuran and 0.2419 g. of ß-naphthol were added to the reaction. The mixture was cooled to -65° using nitrogen pressure to equilibrate the gas burette. Fluoboric acid, 0.55 ml. (40% aqueous solution), was added, and the solid addition tube

* Since the hydrolysis of cis or trans-1,2-diphenylvinyl acetate does not produce diphenylacetylene (39), the diphenylacetylene already present in the reaction mixture was used as the internal standard in this GLC analysis.

was inverted. No gas evolution or color changes were observed so the reaction mixture was disconnected from the gas burette and slowly warmed to 0^{o}. At this temperature gradual gas evolution was observed. The solvent was removed under vacuum at room temperature and the resulting mixture was analysed for products using TLC. Diphenylacetylene and desoxybenzoin were obtained. The identity of both was established by isolation and comparison of the IR spectra to the spectra of authentic samples. GLC showed the presence of peaks with retention times identical to those of authentic diphenylacetylene (64%) and desoxybenzoin (28%).

Attempted interception of vinyl diazo intermediate with dimethyl fumarate.--*A dry three neck flask was fitted with 0.2000 g. of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene, 1.0000 g. of dimethyl fumarate and 15 ml. of dry benzene. To this solution was added 0.040 ml. of dry acetic acid. The reaction mixture was stirred at room temperature for two days and taken to dryness at room temperature under vacuum. No new products in sufficient amounts to be identified could be isolated by TLC. Diphenylacetylene (84%) was found and identified by IR comparison to the spectrum of an authentic sample. The yield of diphenylacetylene found in the decomposition in the absence of dimethyl fumarate was 85 percent. A sample of the decomposition mixture was placed on a hot stage for five minutes to convert any nitrogen containing material to the cyclopropyl compound. TLC of the heated material and the non-heated material from the decomposition showed the presence of trace amounts of the same two compounds of identical R_F value when run side by side on the same plate.

* For a summary of the trapping experiments see Table III.

GLC showed the presence of diphenylacetylene but no new products when the heated and non-heated materials were analysed. Thus no vinyl diazo intermediate has been intercepted under the reaction conditions.

Preparation of acetanilide under reaction conditions.--Aniline, 0.1500 g., was stirred with 7 ml. of the same acetic acid that was used in the decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene with acetic acid. After stirring for twenty-four hours at room temperature the solvent was removed under vacuum at room temperature and the resulting solid was analysed by IR. The IR spectrum of the product was superimposible on a spectrum of authentic sample. Acetanilide had been produced under reaction conditions.

Typical acetic acid stability of the products resulting from the decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene.--*The stability of each of the probable reaction products to the reaction medium was determined. A sample of diphenylacetylene was treated with dry acetic acid at room temperature for twenty-four hours. Since trace amounts of mercury vapor from the gas burette could catalyze the addition of acetic acid across the triple bond of diphenylacetylene (22), the stability test reaction was connected to the gas burette. Diphenylacetylene was quantitatively recovered from the reaction solvent by removal of the solvent under vacuum. An IR spectrum of the recovered compound was superimposible on a spectrum of authentic material. GLC of the recovered diphenylacetylene showed that the purity of the compound was not affected by treatment with the reaction solvent, since no

* The concentrations of materials tested were approximately the same as found in the decomposition reactions.

other peaks were observed.

A sample of desoxybenzoin was treated with dry acetic acid at room temperature and recovered quantitatively after twenty-four hours by removal of the solvent under vacuum. An IR spectrum of the recovered compound was superimposible on a spectrum of authentic sample. GLC of the recovered desoxybenzoin showed that the purity of the material was not affected, since no other peaks were observed.

Diphenylacetaldehyde was treated with the decomposition solvent at room temperature for twenty-four hours. It was recovered quantitatively from the reaction solvent by removal of the solvent under vacuum. An IR spectrum of the recovered diphenylacetaldehyde was superimposible on a spectrum of authentic sample. GLC of the recovered diphenylacetaldehyde showed the material to be pure. Diphenylacetaldehyde was not affected by the reaction solvent.

A sample of hydrobenzoin diacetate was treated with the decomposition solvent at room temperature for twenty-four hours. It was recovered quantitatively from the reaction solvent by removal of the solvent under vacuum. The NMR spectrum of the recovered diacetate was identical to the spectrum of the original sample.

A sample of 2,2-diphenylvinyl acetate was treated with dry acetic acid at room temperature and recovered quantitatively after twenty-four hours by removal of the solvent under vacuum. The IR spectrum of the recovered material was superimposible on a spectrum of authentic sample. GLC of the recovered 2,2-diphenylvinyl acetate showed that no new compounds had been produced and that this acetate was stable to the reaction conditions.

Trans-2,2-diphenylvinyl acetate* was treated with glacial acetic acid at room temperature for twenty-four hours. It was recovered quantitatively from the decomposition solvent. An IR spectrum of the recovered trans acetate was superimposible on the spectrum of an authentic sample. GLC of the material showed the presence of a peak that had a retention time identical to that of authentic trans-1,2-diphenylvinyl acetate but no other material was present.

A mixture of cis-1,2-diphenylvinyl acetate and desoxybenzoin was treated with glacial acetic acid at room temperature for twenty-four hours. The mixture was analysed by GLC after removal of the solvent under vacuum. The ratio of peak areas was the same for both compounds, before and after treatment with the reaction solvent, and no new compounds were observed. Since desoxybenzoin is stable to the acetic acid decomposition medium, and the ratio of desoxybenzoin and cis acetate was the same before and after treatment with the reaction solvent, it follows that cis-1,2-diphenylvinyl acetate is also stable to glacial acetic acid at room temperature.

A sample of the acetic acid decomposition reaction of the triazene using glacial acetic acid at room temperature was subjected to GLC after removal of the solvent under vacuum. The ratios of the peak areas were determined and the mixture was set aside for three days. GLC was again used to determine the ratios of the peak areas. No changes in the peak area ratios were observed and the stability of the reaction products to

* A rigorous identification of the cis and trans isomers of 1,2-diphenylvinyl acetate was not made, but the experimental evidence which was gathered supports the assignment that was made.

the glacial acetic acid reaction medium is assured.

A similar series of stability tests was conducted using the 20 percent acetic anhydride in acetic acid reaction medium and using 87.5 percent aqueous acetic acid medium. All of the materials were recovered quantitatively after twenty-four hours by removal of the solvent under vacuum.

A sample of desoxybenzoin was treated with deuterated acetic acid-acetic anhydride reaction solvent at room temperature for twenty-four hours. Desoxybenzoin was recovered quantitatively from the reaction solvent by removal of the solvent under vacuum. The IR spectrum of the material that had been treated with deuterated acid was similar to the spectrum of an authentic sample. GLC showed the presence of a compound with a retention time identical to that of authentic desoxybenzoin. No other materials were observable by GLC. An NMR spectrum of authentic desoxybenzoin exhibited a phenyl multiplet at 2.7τ and a sharp singlet for the benzylic hydrogens at 5.78τ. The NMR spectrum of the desoxybenzoin that had been treated with the deuterated solvent exhibited a phenyl multiplet at 2.7τ and a poorly resolved pair of singlets at 5.7τ and 5.79τ. Desoxybenzoin has incorporated deuterium in the benzylic position as shown by the NMR spectrum. The IR spectra and the GLC data show that desoxybenzoin has not been altered in any other way.

A sample of trans-1,2-diphenylvinyl acetate was treated with deuterated acetic acid in acetic anhydride at room temperature for twenty-four hours. Trans-1,2-diphenylvinyl acetate was quantitatively recovered from the reaction solvent after the removal of solvent under vacuum. The IR spectrum of the recovered material was superimposible

on a spectrum of authentic sample. GLC showed the presence of a compound with retention time identical to that of authentic acetate. No other peaks were observed by GLC. The NMR spectrum of the acetate exhibited a phenyl multiplet at 2.6τ , a vinyl singlet at 3.32τ and a methyl singlet at 7.76τ . The ratio of methyl to vinyl hydrogens was 3:1 before and after treatment with deuterated solvent. The results of the stability tests indicate that trans-1,2-diphenylvinyl acetate is completely stable to the reaction solvent and does not incorporate deuterium in the vinyl position under reaction conditions.

Since a sample of pure cis-1,2-diphenylvinyl acetate was not available, a sample of a mixture of cis and trans-1,2-diphenylvinyl acetate and desoxybenzoin was analysed by NMR. The spectrum exhibited vinyl hydrogens at 3.32τ (trans-acetate) and at 3.55τ (cis-acetate) in identical ratios before and after treatment with deuterated solvent. It has been independently shown that the trans acetate did not incorporate vinyl deuterium from the deuterated reaction solvent. Therefore, it follows that the NMR spectrum has shown that cis-1,2-diphenylvinyl acetate does not incorporate deuterium in the vinyl position under reaction conditions.

Decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene with acetic acid.--A dry three neck flask was fitted with a gas burette, septum, stirring bar and a solid addition tube containing 0.5000 g. (0.00123 moles) of 1-(triphenylethenyl)-3-phenyl-1-triazene. Seven ml. of dry acetic acid was added, the stirrer was started and the gas burette was equilibrated. After equilibration, the solid addition tube was inverted. Gas evolution (31.0 ml.) was complete within a minute. The

mixture was taken to dryness at room temperature under vacuum and the resulting solid was subjected to TLC. Two components were present. Separation was accomplished by fractional crystallization from petroleum ether, b.p 65-110°. The first component quantitatively accounted for the triphenylvinyl entity and was identical in m.p. and mixed m.p. to a sample of authentic triphenylvinyl acetate. Its IR spectrum was superimposible on a spectrum of authentic triphenylvinyl acetate. The second component was likewise compared with authentic acetanilide and found to be identical.*

Decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene with sulfuric acid.--A sample of 1-(triphenylethenyl)-3-phenyl-1-triazene was added with stirring to 98 percent sulfuric acid, which had been cooled to 10°. Gas evolution was complete with five minutes. The tan paste was stirred at 10° for an additional ten minutes and poured over ice. The organic material was extracted with ether. After removal of the ether, with a stream of nitrogen, a light tan solid was obtained. An IR spectrum of the solid was compatible with a spectrum of authentic phenyl benzhydryl ketone.

A sample of the tan paste was poured over a slush of cold glacial acetic acid. The organic material was again extracted with ether, washed well with water and dried over magnesium sulfate. The ether was removed with a stream of nitrogen. An IR spectrum of the solid residue exhibited all of the peaks present in a spectrum of phenyl benzhydryl

* Triphenylethyleneglycol diacetate and phenyl benzhydryl ketone were submitted to reaction conditions and found to be stable.

ketone and also all of the peaks present in a spectrum of triphenylvinyl acetate. The identity of both was established by isolation and comparison of the IR spectra to the spectra of authentic samples.

Decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene with p-toluenesulfonic acid.--Dimethyl sulfoxide, 3.5 ml., and water, 3.5 ml., were mixed at room temperature. To this solution was added 1.170 g. of p-toluenesulfonic acid. A gas burette was attached, and the flask was fitted with septum and a solid addition tube containing 0.5000 g. of 1-(triphenylethenyl)-3-phenyl-1-triazene. After equilibration, the solid addition tube was inverted. Gas evolution (30.8 ml.) was complete within three hours. Ether was added and the organic layer was washed with water till neutral and dried over magnesium sulfate. Preparative TLC was used to isolate phenyl benzhydryl ketone (91.5% yield). The decomposition product ketone was identical in m.p. and mixed m.p. to an authentic sample. An IR spectrum of the decomposition ketone was superimposible upon a spectrum of authentic phenyl benzhydryl ketone. The second compound was also isolated by preparative TLC. This new compound, m.p. 153°, had an IR spectrum with absorptions at 6.25, 7.3 and multiplet at 8.4-8.6 μ., which is characteristic of sulfonate esters (44). The new compound hydrolyzed to p-toluenesulfonic acid and a ketone which had an IR spectrum that was superimposible on an IR spectrum of authentic phenyl benzhydryl ketone, when treated with aqueous ethanolic hydrochloric acid. The maximum yield of sulfonate ester isolated was 25 percent using 1.170 g. of p-toluenesulfonic acid mono-hydrate, 1.305 g. of commercial sodium p-toluenesulfonate and 7.0 ml. of dimethyl sulfoxide as the reaction medium.

Anal. Calcd. for $C_{27}H_{22}SO_3$: C, 76.04; H, 5.20. Found: C, 76.25; H, 5.40.

Decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene with phenol.-An attempt to intercept a vinyl diazonium ion with phenol.--A dry three neck flask was fitted with a septum, stirring bar, gas burette and a solid addition tube containing 0.5000 g. of 1-(triphenyl-ethenyl)-3-phenyl-1-triazene. A solution of 1.1562 g. of phenol in 7 ml. of dry ether was cooled to -70° using nitrogen pressure to equilibrate the gas burette. The solid addition tube was inverted. No gas evolution or color change was noted. The gas burette was disconnected and the reaction was gradually warmed to 0°. After gas evolution was complete, the mixture was taken to dryness at room temperature under vacuum. Preparative TLC showed that only one compound new was present in sufficient quantity to be identified. It was obtained as a solid, m.p. 165°, after crystallization from alcohol. The IR spectrum exhibited peaks at 6.25 and 8.3 μ., which is compatible with a vinylic aryl ether (45). The aryl ether accounted for 65 percent of the triphenylvinyl entity.

Phenyl benzhydryl ketone, 35 percent was isolated by preparative TLC. The decomposition ketone had an IR spectrum that was superimposible on a spectrum of authentic phenyl benzhydryl ketone. TLC showed the presence of two additional materials, in amounts too small to be identified. An independent experiment carried out at room temperature showed the presence of trace amounts of two materials with the same R_F values as the two compounds that were found in the decomposition which was run at C°. The independent experiment also showed that nitrogen evolution had been complete and therefore neither could have contained the diazo linkage. Since the decomposition at room

temperature, where diazonium ion capture is less likely, gave the same two materials as the decomposition at 0°, where diazonium ion capture is more probable, and since the triphenyl entity had been totally accounted for by the amount of phenyl benzhydryl ketone and the amount of triphenylvinyl phenolate present, it was concluded that the diazonium ion was not captured under these experimental conditions.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.97. Found: C, 89.45; H, 5.89.

Decomposition of 1-(triphenylethenyl)-3-phenyl-1-triazene with p-toluenesulfinic acid.--To 10 ml. of dimethylformamide in a three neck flask was added 1.9188 g. of p-toluenesulfinic acid and 2.1894 g. of sodium p-toluenesulfinate. The flask was fitted with a gas burette, septum, stirring bar, and a solid addition tube containing 0.5000 g. of 1-(triphenylethenyl)-3-phenyl-1-triazene. After equilibration the solid addition tube was inverted. Gas evolution, 31.8 ml., was complete within ten hours. After gas evolution had ceased, the organic layer was taken up in ether and washed well with sodium bicarbonate solution and water till neutral. The ether layer was dried over magnesium sulfate and concentrated to an oil. Two compounds were found by preparative TLC. The first had an IR spectrum that was identical to a spectrum of authentic phenyl benzhydryl ketone. The second component, an oil, had an IR spectrum that exhibited peaks at 6.3, 7.5, 8.8 and 9.0 μ., which strongly suggests a vinyl sulfone (V) (46).

Preparation of triphenylvinyl acetate, triazene method.--Triphenylvinylbromide, 1.0000 g. (0.002965 moles), was dissolved in 15 ml. of dry ether and added to a reaction flask fitted with stirring bar, condenser, and a septum sealed dropping funnel, that had been charged with 0.0720 g.

(0.002965 moles) of magnesium and a crystal of iodine. The mixture was brought to reflux. After the magnesium had been consumed, 0.3530 g. of phenyl azide in 5 ml. of dry ether was added dropwise. The reaction was stirred for one hour at room temperature and treated with 25 ml. of stock ammonium chloride-ammonia solution. The ether layer was separated and dried over magnesium sulfate. The ethereal solution was placed in an pressure equalizing dropping funnel fitted with a drying tube and added dropwise with stirring at room temperature to 15 ml. of dry acetic acid. After gas evolution was complete, the reaction was concentrated to dryness at room temperature under vacuum and subjected to preparative TLC. Eighty-five percent of the theoretical triphenylvinyl acetate was isolated. It was identical in m.p., mixed m.p. and its IR spectrum was identical to an authentic sample.

Decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with acetic acid.--To 7 ml. of dry acetic acid in a flask fitted with a gas burette, stirring bar, and a solid addition tube was added 0.5000 g. of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene. Gas evolution (29.3 ml.) was complete within minutes. The reaction mixture was taken to dryness at room temperature under vacuum. TLC showed two products. The first, isolated by fractional crystallization from petroleum ether, b.p. 65-110°, had an IR spectrum that was identical to a spectrum of authentic acetanilide. The second compound accounted for 88 percent of the phenylvinyl entity. It had a m.p. of 85-7° after crystallization from petroleum ether. The IR spectrum of this second compound exhibited peaks at 3.3, 5.7, 6.3 and 8.3 μ., which is compatible with di-p-tolylphenylvinyl acetate (47).

Anal Calcd. for $C_{24}H_{22}O_2$: C, 84.18; H, 6 48. Found: C, 84.00; H, 6.65.

Ozonolysis of di-p-tolylphenylvinyl acetate.--A sample of the crude product formed in the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with acetic acid was dissolved in 5 ml. of ethyl acetate and ozonized as previously described. After drying over magnesium sulfate, the ether was removed with a stream of nitrogen and the mixture was analysed by GLC. Two compounds were present in the ratio of 4:1. The major component had a retention time identical to that of authentic di-p-tolyl ketone. The minor component had a retention time identical to that of authentic p-methylbenzophenone. IR analysis of the mixture gave a spectrum that was superimposible on the spectrum of a 4:1 mixture of di-p-tolyl ketone and p-methylbenzophenone. Thus, the major acetate formed in the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene was the non-rearranged acetate and the minor acetate was rearranged di-tolyl acetate.

Decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with p-toluenesulfinic acid.--A solution of 4.25 ml. of dimethylformamide, 0.7727 g. of p-toluenesulfinic acid and 0.8500 g. of sodium p-toluenesulfinate was prepared in a three neck flask fitted with a gas burette, stirring bar, septum and a solid addition tube containing 0.2000 g. of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene. After equilibration, the solid addition tube was inverted. Gas evolution, 30.2 ml., required ten hours. The mixture was put into water, and the organic material was extracted thoroughly with ether. The ether layer was washed thoroughly with sodium bicarbonate and water. After drying over magnesium sulfate the ether was evaporated with a stream of nitrogen and the reaction mixture was analysed by preparative TLC.

Two components were present. The first, an oil, had an IR spectrum that exhibited peaks at 6.3, 7.5 and 8.7 μ., which strongly suggests the presence of a vinyl sulfone (XI) (46). The second, present in small amounts, had an IR spectrum that was very similar to phenyl benzhydryl ketone.

Ozonolysis of di-p-tolyl-phenylvinyl-p-tolyl sulfone.--A sample of the mixture formed in the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with p-toluenesulfinic acid was dissolved in 5 ml. of ethyl acetate, and ozonized as previously described. The reaction mixture was analysed by GLC. A peak was present that had a retention time identical to that of authentic di-p-tolyl ketone but no peak was present that had a retention time identical to that of p-methylbenzophenone. It was estimated that an amount of p-methylbenzophenone corresponding to 1/100 of the amound of di-p-tolyl ketone known to be present would have been easily visible. An IR spectrum of the ozonolysis product exhibited all the peaks present in a spectrum of authentic di-p-tolyl ketone.

Typical ozone stability test of the products resulting from the decomposition of 1-(2,2-di-p-tolyl-phenylethenyl)-3-phenyl-1-triazene with acid.--Acetanilide, 0.1000 g., was dissolved in 5 ml. of ethyl acetate, cooled to 0°, and treated with ozone for fifteen minutes. The solvent was removed with a rotary evaporator and the solid was subjected to IR analysis. The spectrum was identical to a spectrum of authentic acetanilide. The remaining solid was treated with 2 ml. of water, a trace of zinc dust and several drops of acetic acid. The mixture was brought to reflux for several hours, cooled, and the organic material

was extracted into ether. The ether layer was washed with sodium carbonate solution and water. After drying over magnesium sulfate, the solvent was removed and the oil was analysed by GLC. The major component had a retention time that was identical to that of authentic acetanilide and no peaks were observed that had retention times that were identical to those of p-methylbenzophenone, di-p-tolyl ketone, benzophenone or acetophenone. An IR spectrum of the solid was compatible with a spectrum of authentic acetanilide. Likewise individually tested were phenyl benzhydryl ketone and α-phenylpropiophenone. These three ketones were also stable to ozonolysis conditions. Thus the cleavage of these materials cannot account for the products found in the ozonolyses of the vinyl products found in the acid triazene decomposition.

Decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene with deuterated acetic acid-acetic anhydride.--A solution, approximately 80 percent deuterated acetic acid in acetic anhydride, was made by warming 3.18 ml. of deuterium oxide and 22.0 ml. of freshly distilled acetic anhydride. Seven ml. of this solution was put into a dry three neck flask fitted with a septum, stirring bar, drying tube and a solid addition tube containing 0.5000 g. of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. The addition tube was inverted and, after gas evolution had ceased, the solution was taken to dryness at room temperature under vacuum. A portion of the mixture was analysed for products using GLC. The following were found: diphenylacetylene (60%), desoxybenzoin (20%), cis-1,2-diphenylvinyl acetate (12.6%), trans-1,2-diphenylvinyl acetate (7.1%), acetanilide, and a trace of 1,1,4,4-tetraphenyl-1,3-butadiene. This trace amount of 1,1,4,4-tetraphenyl-1,3-butadiene was also present

in the starting triazene. A portion of the mixture was subjected to preparative TLC and 0.0089 g. of slushy oil was obtained. GLC of the oil showed the presence of desoxybenzoin, cis-1,2-diphenylvinyl acetate and trans-1,2-diphenylvinyl acetate in a ratio of 2:4:2. The mixture was analysed by NMR using phenylacetylene as an internal analytical standard. A multiplet was observed from 2.3 to 3.1τ. A poorly resolved pair of singlets were observed at 5.7 and 5.79τ. Two singlets were observed at 6.93* and 7.83τ. No peaks were observed from 3.1 to 4.0τ. It was estimated that 5 percent of vinyl hydrogen would have been easily observable in the spectrum. Thus cis and trans-1,2-diphenylvinyl acetate have undergone complete deuterium incorporation in the vinyl position.

Decomposition of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene with acetic acid-acetic anhydride.--A solution, approximately 80 percent acetic acid in acetic anhydride, was made by warming 3.18 ml. of water and 22.0 ml. of freshly distilled acetic anhydride. Seven ml. of this solution was used to run a non-deuterated control decomposition of 0.5000 g. of 1-(2,2-diphenylethenyl)-3-phenyl-1-triazene. The following products were found by GLC: diphenylacetylene (59%), desoxybenzoin (21%), cis-1,2-diphenylvinyl acetate (12.5%), trans-1,2-diphenylvinyl acetate (8.0%), acetanilide and a trace of 1,1,4,4-tetraphenyl-1,3-butadiene. A portion of the mixture was subjected to preparative TLC. GLC showed a mixture of desoxybenzoin, cis-1,2-diphenylvinyl acetate and trans-1,2-diphenylvinyl acetate in the ratio of 3:2:1. A 0.0089 g. sample of this oil was

* The literature reports the acetylenic hydrogen in phenylacetylene is found at 6.95τ (48).

analysed by NMR using phenylacetylene as an internal analytical standard. A singlet was observed at 3.55τ which was twice as large as a singlet at 3.32τ. In addition, a singlet was present at 5.79τ, another singlet was observed at 6.94τ, and a singlet was observed at 7.80τ. The control experiment shows that the yields of products were not significantly affected by the deuterated solvent.

Decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene with acetic acid.--A dry three neck flask was fitted with a septum, stirring bar, gas burette, 2 ml. of dry acetic acid and a solid addition tube containing 0.1000 g. of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene. After equilibration, the solid addition tube was inverted. Gas evolution (6.1 ml.) was complete within minutes. The solvent was removed at room temperature under vacuum. GLC showed acetanilide and three other components in the ratio of 2:3:25.* An IR spectrum of the mixture exhibited all of the peaks present in a spectrum of authentic acetanilide. In addition, the spectrum exhibited peaks at 3.3, 3.5, 5.7, 6.25 and 8.3 μ. Preparative TLC was used to separate the major component. An IR spectrum of the resulting oil exhibited peaks at 3.3, 3.5, 5.7, 6.25 and 8.3 μ., which is compatible with diphenylmethylvinyl acetate (XIVa,b) (47). GLC showed slight contamination with both of the minor components.

Ozonolysis of diphenylmethylvinyl acetate from the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene with acetic acid.--Five

* Later experiments showed that one of the two minor components was α-phenylpropiophenone. The other minor component and the major components were the isomeric diphenylmethylvinyl acetates.

ml. of ethyl acetate was added to a portion of the mixture from the acetic acid triazene decomposition. The mixture was ozonized as described previously, and analysed by GLC. Two ketones were present in the ratio of 10:1. The major ketone had a retention time identical to that of authentic acetophenone. The minor ketone had a retention time that was identical to that of benzophenone. An IR spectrum of the mixture of ketone decomposition products was compatible with a spectrum of a mixture of authentic samples. GLC showed a peak with retention time identical to that of one of the minor components originally present in the acetic acid decomposition reaction but no peak was present with retention time of either major component.*

Hydrolysis of diphenylmethylvinyl acetate from the decomposition of 1-(2,2-diphenyl-methylethenyl)-3-phenyl-1-triazene.--A portion of the decomposition mixture isolated by removal of solvent under vacuum, as described above, was refluxed for two hours with 4 ml. of ethanol, 0.4 ml. of water and 0.5 ml. of hydrochloric acid. After cooling, the mixture was poured into water and the organic material was thoroughly extracted with ether. The ether layer was dried over magnesium sulfate. The solvent was removed with a stream of nitrogen and the resulting oil was analysed for products. GLC showed a component that had a retention time identical to that of one of the minor components in the original acetic acid decomposition. The IR spectrum of the material exhibited peaks at 3.3-3.5 and 5.95 μ., which is compatible with a phenyl ketone (49).+

* This minor component was later identified as α-phenylpropiophenone which is stable to ozonolysis conditions.
+ A second very small carbonyl peak was observed at 5.8 μ., which was taken as evidence of contamination by 1,1-diphenylacetone.

The NMR spectrum exhibited a multiplet at 2.75τ , a quartet at 5.32τ and a doublet at 8.47τ , which is compatible with α-phenylpropiophenone. The weight of the oil represented an 89 percent recovery of the diphenylmethylvinyl entity.

Preparation of 9-bromomethylenefluorene.--This compound was prepared by bromination of fluorenylideneacetic acid, available by the procedure of Sieglitz and Jassoy (50) or Hauser and Lednicer (51), followed by decarboxylative dehydrobromination as described by DeTar (52). The product was purified by chromatography on silica gel using ether-pentane as the eluent and obtained as a colorless solid, m.p. 71-3° (82% yield). The literature (52) reports m.p. 72.5-73°, and a yellow product in(87% yield).

Preparation of bromo-2,2-dimethyl-phenylethylene.--The preparation of 1, 1-dimethyl-phenylethylene was accomplished by an adaptation of the preparation of triphenylethylene (27) using benzaldehyde and isopropyl bromide. The substituted ethylene was distilled, b.p. 50°/ 2.3 mm. (84% yield), and obtained as a colorless oil (53) (lit. b.p. 76-7°/ 11 mm). The substituted ethylene was brominated in acetic acid and dehydrohalogenated by refluxing the acetic acid solution of the dibromide for several hours. The reaction mixture was concentrated with a rotary evaporator, poured into water, and the organic material was extracted into ether. The ether layer was washed with water till neutral and dried over magnesium sulfate. The product was distilled, b.p. 120°/ 5 mm. (91% yield), and obtained as a pale yellow oil. The IR spectrum was compatible with the proposed structure (54). The UV spectrum showed absorption characteristic of styrene-like molecules (55).

Attempted preparation of 9-bromomethylene-10-xanthene.--The preparation of this compound was attempted by the bromination of 9-xanthylidene-acetic acid, which was synthesized by an adaptation of the procedure of Sieglitz and Jassoy (50). Decarboxylative dehydrobromination of the crude brominated acid was attempted by the method of DeTar (52). No 9-bromomethylene-10-xanthene was found. These results are in accord with previous synthetic difficulties in this system as reported by Goldberg and Wragg (56).

Attempted preparation of bromomethylenecyclopentane.--Attempts to prepare bromomethylenecyclopentane by the method of Wolinsky and Erickson (57) using bromomethyltriphenylphosphonium bromide and cyclopentanone led to low yields of bromomethylenecyclopentane.* Since this compound was intended for use as an intermediate in the preparation of 1-(2-tetramethylene-ethenyl)-3-phenyl-1-triazene, this portion of the project was abandoned.

Attempted preparation of 1-(2-pentamethylene-ethenyl)-3-phenyl-1-triazene.--The method of Wallach (58) was used to prepare bromomethylenecyclohexane (57). The first attempts to prepare the triazene by treatment of the bromide with magnesium and phenyl azide as described earlier for the preparation of the diphenyl triazene (X) failed, and this portion of the project was abandoned.

Attempted preparation of 1-(9-methylenefluorenylidene)-3-phenyl-1-triazene.--A dry three neck flask was fitted with a condenser and a

* For a recent article discussing the problems associated with the syntheses of bromomethylenecycloalkanes see (57) and references therein cited.

septum sealed dropping funnel. The flask was swept with nitrogen and charged with 0.0945 g. (0.00389 moles) of magnesium turnings and a stirring bar. To this was added 10 ml. of dry tetrahydrofuran and a crystal of iodine. A solution of 1.000 g. (0.00389 moles) of 9-bromomethylenefluorene in 15 ml. of dry tetrahydrofuran was added dropwise with stirring. When the mixture was heated to reflux, it turned deep green and finally purple. The magnesium was consumed in two hours. When the reaction cooled to room temperature, the purple color faded, and a solution of 0.464 g. (0.00389 moles) of phenyl azide in 10 ml. of dry tetrahydrofuran was added dropwise with stirring. Ether was added followed by 30 ml. of stock ammonium chloride-ammonia solution. An orange precipitate immediately formed which was insoluble in both layers. Filtration yielded 0.620 g. of orange solid which gave no qualitative test for nitrogen (59), and had a m.p. of 360° with sublimation. Kuhn and Winterstein report (60) that 1,2-(di-9-fluorenylidene)-ethane has a m.p. of 360° with sublimation. The 0.620 g. represents 90 percent recovery of the fluorenylidene entity. Experimental modifications were unsuccessful and yielded nothing but dimer, unreacted phenyl azide and minor amounts of non-nitrogen containing by-products. Ether yielded only starting bromide and varying amounts of dimer depending on the total reflux time. Butyllithium in ether at dry ice temperatures gave only dimer using the normal addition order.

Attempted preparation of 1-(2,2-dimethyl-phenylethenyl)-3-phenyl-1-triazene.--The method described earlier for the preparation of the diphenyl triazene (X) was adapted for the preparation. The resulting oil resisted all attempts at crystallization. TLC indicated a mixture of products. The crude oil was put into a pressure equalizing dropping

funnel that was sealed with a septum and added dropwise with stirring to 10 ml. of dry acetic acid in a three neck flask fitted with septum, gas burette and a magnetic stirring bar. The mixture evolved a maximum of 5 ml. of nitrogen over a one hour period. (By analogy to previously synthesized triazenes, less than 2 percent of the desired triazene could have been present. No attempts to isolate products were made.) Furthermore, an NMR spectrum of the drude oil before acid treatment showed no peaks in the 3.1-4.2τ region, which suggests that the Grignard reagent had dimerized before it could react with phenyl azide. Similar results were obtained in the attempted preparation of 1-(9-methylenefluorenylidene)-3-phenyl-1-triazene. An IR spectrum of the oil obtained in the attempted preparation exhibited a strong absorption at 4.74 μ., which is compatible with the presence of unreacted phenyl azide (30). On one occasion a few crystals of white solid, m.p. 155-60°, were obtained. These crystals did not effervesce when treated with acid or when heated and gave no qualitative test for nitrogen (59). An IR spectrum of the solid showed no absorption in the carbonyl region, which was taken as evidence that the solid was not an aqueous decomposition product of the desired 1-(2,2-dimethyl-phenylethenyl)-3-phenyl-1-triazene. This portion of the project was abandoned.

Attempted preparation of 1-(phenylethynyl)-3-phenyl-1-triazene.--A dry three neck flask was fitted with a condenser, a septum sealed dropping funnel and a magnetic stirring bar. The flask was charged with 1.2150 g. (0.050 moles) of magnesium, 100 ml. of dry ether and a crystal of iodine. Ethyl bromide, 5.4500 g. (0.505 moles), was added dropwise with stirring. After the magnesium had been consumed, 5.100 g. (0.050 moles)

of phenylacetylene was added and the solution was refluxed over night (34). The reaction mixture was cooled to room temperature and 5.960 g. (0.050 moles) of phenyl azide in 10 ml. of dry ether was added dropwise with stirring. The reaction, now a deep green, was treated with 50 ml. of stock ammonium chloride-ammonia solution. The ether layer was separated and dried over magnesium sulfate. The ether layer was concentrated to approximately 25 ml. total volume with a stream of nitrogen and refrigerated. A white solid was filtered off and washed well with cold pentane. The solid, m.p. 113-4° with no effervescence (85% yield), did not effervesce when treated with dry acetic acid. The IR spectrum exhibited a broad peak at 2.9 μ., but exhibited no peak in the acetylenic region (54). The UV spectrum exhibited a maximum at 248 mμ. The NMR spectrum exhibited a peak at 2.19τ and a phenyl multiplet at 2.7τ. These data are consistent with 1,5-diphenyl-1,2,3-triazole (61). The literature reports m.p. 113-4° for the triazole which was prepared by the reaction of phenyl azide and phenylacetylene.

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BIOGRAPHICAL SKETCH

Frederick William Miller was born in Burke, South Dakota, on May 19, 1938. He is the son of Rev. and Mrs. Fritz H. Miller, who presently live in La Crosse, Wisconsin. After his graduation from Wisconsin State University in 1960 with a Bachelor of Science degree, he taught at Luther High School, Onalaska, Wisconsin. He later moved to Waukegan, Illinois, where he worked as a Research Assistant in Organic Chemistry at Abbott Laboratories, North Chicago, Illinois.

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This dissertation was prepared under the direction of the chairman of the Candidate's committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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